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Some studies on the reaction mechanism of pack carburization

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NOTE TO USERS

SOME STUDIES ON THE REACTION MECHANISM OF PACK CARBURIZATION

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I. INTRODUCTION

The process by which the carbon content of the metal near the surface of a piece of iron or steel is increased without subjecting the metal to fusion is termed carburizing or case hardening. By the middle of the sixteenth century the art of case hardening was being used in making weapons by heating the part to be hardened in a mixture of charcoal and organic substances. Some of the first researches on the carburizing process were to study the possibility of the direct interaction of the solid carbon with the steel. Giolitti (1, pp. 116-125) concluded that while some carburization by direct contact may occur, particularly under extremely intimate contact, the action is so slight as to be of no practical importance. This conclusion has been accepted, without further experimental verification, by recent writers (2, 3, 4) and some (5, 6) seem to imply that the direct action cannot take place. Among the few writers that allow for a possibility of some measurable degree of direct action between the carbon and iron is Grossmann (7, p. 428) who has stated: "It seems clear from many experiments that pack carburizing takes place through the formation of carbon monoxide gas which in turn reacts with the steel, although this does not exclude the possibility that carbon might carburize iron under proper conditions of intimate contact." The purpose

of part of the work reported in this thesis was not to disprove the gas theory, but to study the direct action of pure sugar carbon on steel in the presence of as little gas as was possible or, in other words, at pressures approaching a true vacuum.

In the fields of gas carburizing and furnace atmospheres a great deal of work has been done on the effect of water vapor. As will be seen throughout the historical section, especially in the latter part where the present theories of pack carburizing are outlined, there has been little or no mention made of water vapor. Lewis (8) pointed out that in the opinion of many metallurgists moisture in the carburizing compound is a source of soft spots in the case and that some go so far as to avoid the shipping of their compounds by water freight. Lewis (8, p. 697) wrote: "It is hard to conceive that small amounts of water vapor heated to some 1700 degrees Fahrenheit in the presence of carbon can remain as steam and do harm to the work." He also stated that he had never been able to trace soft spots to absorbed moisture in carburizing compounds. Sutton and Ragatz (9) expressed the same view in regard to the presence of moisture in carburizing compounds. Webber (10) reported an experiment in which he soaked charcoal in water and allowed it to drain before using it as a pack in a commercial carburizing box. He heated iron packed in this charcoal to 800° C. and obtained increased decarburization which he said was due

to the hydrogen formed by the reaction $2H_2O + C = 2H_2 + CO_2$. Webber concluded from this experiment that extreme care must be taken to remove moisture from the atmosphere even in the presence of carbon. His experiment has little bearing on the point in question, however, because of the very large amount of moisture and the low temperature which he used.

Since there was doubt as to the effect of small amounts of water vapor on the carburization reaction, it seemed advisable to perform a series of experiments using dry air and air saturated with water vapor at room temperature. Both plain sugar charcoal and a pack containing 15 o/o barium carbonate were used in this part of the investigation.

Two fairly independent phases of the mechanism of carburization have thus been investigated and the results reported here. One of these investigations deals with the direct action of carbon and iron, or vacuum carburization. The other part of this report is the result of a study of the part played by water vapor in ordinary pack carburization.

II. HISTORICAL

Although the process of carburization was employed as early as 1556, the first researches carried out to determine the nature and cause of the process date from the beginning of the eighteenth century when, as pointed out by Giolitti (1, p. 3), Reaumur started a systematic study of various carbonaceous materials then employed in case hardening. The purpose of his work was to find the best material to use in carrying out the hardening process, although in some of his work he attempted to ascertain the cause of carburization. Reaumur was one of the first investigators to show that a piece of iron increased in weight upon being carburized.

During the latter part of the eighteenth century the subject of the mechanism of the carbon enrichment began to receive considerable attention. There were two trains of thought in regard to this question, one dealing with the action of gases and the other with the direct interaction of the carbon with the iron or steel. The latter idea was the most important at the beginning of the investigations. The use of a vacuum and the use of gases, such as hydrogen and nitrogen, were the two approaches used to study this problem. Nitrogen and hydrogen, which were considered inert, were used to displace all other gases present, or in other words,

they were used as a substitute for vacuum conditions. Interpretation of the correctness of the results obtained by many of the early investigators is difficult because of the manner in which the experimental conditions, such as temperature, pressure, and purity of materials were reported.

As reviewed by Guyton de Morveau (11), Clouet in 1799 heated an iron crucible containing diamond to bright red heat and obtained an increase in weight of the crucible, which he accounted for by the direct penetration of the carbon into the iron of the container. Obviously his investigation suffers from the fact that the gases from the furnace were not excluded from the crucible. Gay-Lussac (12) stated in his paper of 1846 that he could see no reason for excluding the possibly that the carbon can act simply by contact, dissolving directly in the iron without the intervention of any gas or vapor. He did not present experimental work of his own, but reasoned from his theory that all substances are capable of reacting with each other when brought into contact, whatever may be their state of aggregation. He admitted, however, that the solid state must be considered the least favorable for the operation of reactions dependent upon chemical affinity. Margueritte (13) was the next investigator to support the theory or supposition of the direct action of carbon on iron or steel. In his work he used an atmosphere of pure dry hydrogen and a temperature of "bright redness". By heating iron with diamond dust,

graphite, or sugar carbon he found that carburization took place. Margueritte justified his use of hydrogen by pointing out that where the iron was not in contact with the carbon there was no apparent carburization.

Giolitti (1, pp. 14-16) summarized the works of Mannesmann who in 1879 began a series of investigations on carburization. In his experiments he attacked the problem of the direct action of carbon on steel by heating together, in the presence of the furnace gases, two steels of different carbon content. He found when the two bars were placed so that they were firmly together the carbon migrated from the bar of higher carbon content to the bar of lower carbon content. In addition to this, he carried out the same experiment with the bars immersed in a molten salt so as to exclude all gases, except, of course, those already present in the metal. The same carbon migration was found to take place. Mannesmann thus concluded from his experiments that the carburizing action is due to solid carbon reacting with the steel and that the carbon migrates into the steel by molecular migration. A few years later Hempel (14) stated that he had been able to prove experimentally that the diamond exercises a carburizing action on iron beginning at a temperature of about 1160° C. In his investigations he used an atmosphere freed from the least trace of oxygen. The criticism of his work is that his temperatures can hardly be considered as being any more than approximate, since he measured them by

using sheets of alloys of gold and platinum fusible at different temperatures. This method of measurement, at its best, can only be approximate. Also, since the temperatures used by Hempel, even though approximate, are very high in comparison to those used in ordinary carburizing and in investigations on carburizing, the data are not very comparable with that obtained by other investigators.

The next work of any importance on the subject of the direct action of carbon on iron or steel was carried out by Roberts-Austen (15) in 1890. He heated electrolytic iron in contact with a diamond in a vacuum (pressures not given) to full-red heat and reported that he obtained carburization. His apparatus was so arranged that both the iron and the diamond could be heated in the vacuum before effecting contact of the two. Roberts-Austen implied that if the intervention of a third substance is necessary to produce carburization, minimum traces of such substances are sufficient and these traces of gaseous substances can still remain occluded in the iron even after careful treatment in a vacuum.

In 1891 Osmond (16) experimented on the action of diamond dust with iron in an atmosphere of pure dry hydrogen. His results indicated that at temperatures between 1035° and 1065° C. carburization took place at the points of contact, and at temperatures between 1085 and 1125° C. the diamond completely dissolved in the iron with the formation of graphite. From these experiments Osmond (16, p. 579)

stated: "the diamond, as such, does not cement iron but first undergoes a molecular transformation which renders it capable of carburizing". However, it is rather difficult to see justification of this conclusion from the small amount of data and observations which he presented.

Garnier (17) studied the direct action of carbon on iron in another manner. He placed a bar of steel in a hole in a bar of retort carbon, and heated both to a temperature between 900° and 1000°C. in a reverberatory furnace. A current of 55 amperes at a potential of 7 volts was then passed through the assembly, the carbon being the positive pole and the steel the negative pole. He reported that in three hours he obtained a case 10 mm. deep. Garnier next substituted for the bar of carbon another bar of steel. Between the two bars of steel was placed a 1 cm. layer of compressed wood charcoal. The experiment was then repeated in the same manner and it was found that only the bar acting as the cathode was carburized. He did not report experiments without the use of the electric current so that his results are not very comparable with those of other investigators. Also, all his work was carried out in the presence of the furnace gases.

After the publications of Osmond (16) and Hempel (14), Roberts-Austen wrote a paper (18) in which he reviewed, along with his own (15), the results of the above workers and concluded that it was proved that the process of

carburizing steel is a true phenomenon of diffusion by contact. Royston (19) in his paper on the relation of carbon to iron at high temperatures reported on the problem of the direct action of carbon and iron. He heated two bars of soft steel, one of 0.15 o/o carbon and one of 0.95 o/o carbon for 12 hours in a vacuum (pressures not given). It was found that when the bars were in contact with each other the carbon migrated from the one of higher carbon content to the one of lower carbon content. No change was observed when the two bars were not in contact with each other. Royston concluded that his experiments proved the hypothesis according to which carbon diffuses into iron by simple difference in concentration and without the necessity of the intervention of gases. Guillet (20) in a review of some of his work on carburization with cements reported that important experiments recently completed had permitted him to establish that sugar carbon, graphite, and wood charcoal can not act by simple solution of the carbon by the iron. In his paper he did not elaborate on the experiments that proved this point. About five years later, Guillet and Griffith (21) published a paper in which they gave a lengthy report of their experiments on the carburization of iron with sugar carbon in a vacuum. They treated their sugar carbon in a vacuum at 1000° C. for a long period of time (exact time not given) and repeated the same procedure for the iron used. Their first experiment was to pack the iron wires in the carbon and heat in a

vacuum at 1000 ° C. for five hours a plate of steel kept in contact with the sugar carbon by a pressure of a few grams. Again they obtained no carburization. The last set of experiments was to use an arrangement whereby they could press the plate against the sugar charcoal by means of a screw, thus obtaining very good contact between the iron and carbon. When heated at 1000° C. for five hours in a vacuum, the plate increased in carbon concentration from 0.08 o/o to 0.32 o/o. The pressure obtained,which they referred to as a vacuum, were not stated, the only statement relative to pressures being that when the charcoal was treated in a vacuum the minimum pressure obtained was 5 cm. of mercury.

About the same time Giolitti (1, pp. 116-125) reported the results of his experiments on carburizing in a vacuum. He used sugar charcoal and an iron of 0.09 o/o carbon. His apparatus was so arranged that it was possible to heat the carbon in the vacuum and then drop the iron into the carbon without interrupting the vacuum. In carrying out the experiment, the charcoal was heated to 1100° C. until the pressure was reduced to 0.5 mm. The apparatus was then filled with pure nitrogen and again evacuated. This operation was repeated three times. The temperature was then lowered to 1000° C., the pressure reduced to 0.5 mm., and the samples dropped into the charcoal. The temperature was held at 1000° C. for three hours, during which time the pressure remained in the vicinity of 0.5 mm. Giolitti stated that

the pressure did not fall below this value because of the slight permeability which the porcelain tube assumed at the high temperature. He wrote that these minimum quantities of air had no influence on the process of carburization. His results indicated that slight carburization was obtained at the points where the carbon adhered to the surface of the iron. The photomicrographs given indicate very shallow and uneven cases. From these results Giolitti concluded that while some carburization may occur, particularly under extremely intimate contact, the action is so slight as to be of no practical importance.

Weyl (22) carried out a series of experiments in an apparatus similar to the one used by Giolitti, but capable of lower pressures. He tested the action of sugar carbon, graphite, and diamond on a steel of 0.06 o/o carbon. The experimental procedure was the same as Giolitti's except that the iron reached a higher temperature in the vacuum before being brought in contact with the carbon. The pressures when using sugar charcoal were about 0.2 mm. instead of 0.5 mm. In the case of the graphite on the diamond the pressures were from 0.10 mm. to 0.05 mm. Weyl obtained very slight carburization, the results being comparable to those of Giolitti.

In 1910 Charpy and Bonnerot (23) published a short paper on their work with sugar carbon, graphite, and diamond dust. They stated that they were unable to detect the

slightest trace of carburization after heating iron in contact with carbon at 1000° C. for a long time in a vacuum (pressures not given). Both the iron and the carbon were heated for a long time in a vacuum before being used.

The works of Giolitti (1, pp. 116-125), Guillet and Griffith (21), and Weyl (22) are the ones most often referred to by present writers, especially Giolitti's summary of the above three papers. This accounts for the general belief today that solid carbon does not react directly with solid iron to any considerable degree at ordinary carburization temperatures.

Even before research on the carburization process was started it was known that when substances such as plants, ashes, and blood were mixed with the charcoal the carburization action was greatly increased. This fact was probably one of the greatest causes for the non-acceptance of the direct contact theory and thus stimulated research along lines involving the role of gases in carburization.

One of the first to propose a theory of carburization involving gases was Caron who in 1860 stated that carburization was due only to the formation of volatile cyanides which were capable of penetrating into the pores of the metal and giving up their carbon. Caron's work is reviewed in detail by Necolardot (24). The experiment upon which Caron based his theory was the heating of iron bars surrounded by wood charcoal while passing a current of dry gaseous ammonia

through the apparatus. He reported that good carburization was obtained. By repeating the experiment using hydrogen, nitrogen, carbon monoxide, or air he obtained no carburization. In order to determine the amount of carburization, Caron studied the grain of the fracture after breaking the specimens. This method would not be very reliable and may account for the results reported, which, especially in the case of carbon monoxide, were soon proved incorrect. Caron also ran experiments with charcoal to which he added carbonates or cyanides. He found that both substances increased carburization and, in order to account for the effect of barium carbonate, he concluded that barium cyanide was formed. The actual detection of a cyanide, however, was not reported. Later experiments by Caron showed that it was possible to carburize iron with pure hydrocarbons in the absence of charcoal. This fact was against his own theory of the cyanide action and he had to admit that certain carburetted compounds can carburize without the presence of cyanides.

During the time that Caron was carrying out his experiments, investigators began to focus their attention on the action of carbon monoxide in the carburization of iron. In a series of papers Margueritte (25) described experiments carried out by heating pure iron in a glazed porcelain tube through which was circulated a current of very pure carbon monoxide. He obtained marked carburization of the iron. It will be remembered that Margueritte (13) also upheld the

direct action of carbon theory. He summarized his results (26, p. 378) by stating: "carburization takes place by means of direct contact and also by the decomposition of a carburetted gas; these two causes of carburization acting simultaneously in the box". In his papers Margueritte reviewed the work of other investigators and accounted for their negative results with carbon monoxide by the fact that they used too slow a current of gas so that the presence of carbon dioxide prevented carburization.

In 1903 Charpy (27, 28) reported the results of his experiments on carburization. His experimental conditions were much better controlled and his results more exact than those reported by most previous investigators. This seems to be true of most of the work done from this time on, since the research men began to interpret their results more in terms of metallographic structure, the carbon content, the increase in weight, and the depth of carbon penetration. Temperatures were also recorded and controlled more carefully. Some of Charpy's most significant experiments were the heating of pieces of iron to various temperatures while passing over them a stream of pure carbon monoxide. He determined the increase in weight, the increase in carbon content by combustion methods, and the amount of carbon dioxide evolved from the furnace. Charpy reported that carburization took place at a temperature as low as 560° C. Since he used wires for his determinations, he could not study the amount of penetration.

Charpy also studied the action of packs made by adding alkaline earth carbonates, oxides of carbon, cyanogen, and potassium cyanide to wood charcoal. In some of his experiments he recognized the fact that carbon diffused into the iron because of a concentration gradient and that the diffusion increased with temperature. Guillet (29) also did some work using packs to which he added potassium dichromate, potassium ferrocyanide, potassium cyanide, potassium carbonate, or barium carbonate. He studied the penetration of the carbon with respect to the temperature and the energizer used. From his papers it is evident that he believed in the cyanide theory of Caron, but offered no good proof to substantiate it.

In 1907 Giolitti began to carry out experiments on carburization which led investigators to start a correlation of ideas and data. Giolitti summarized his work in Chapter IV of his book (1, pp. 358-390). One of the first set of experiments carried out by him was on the distribution of carbon in the case. He used chemical analysis and metallographic methods in studying the effect of energizers, time, and temperature on this distribution. His results are among the first of any value to be obtained on this subject. In this work he was the first to actually determine the existence of well defined zones (hypereutectoid, eutectoid, and hypoeutectoid) in the carburized portion of the specimen. Giolitti and his co-workers did a great deal of work on the relation of carbon monoxide to carburization. Their work

showed that Caron's cyanide theory was wrong, and that in ordinary pack carburizing the presence of carbon monoxide played an important role. They proved that the presence of cyanides was not necessary for carburization to take place and also they could not detect the presence of traces of cyanides in the carburizing box when using carbonates as energizers. Giolitti gave no explanation for the energizing action of certain cyanides. In a series of experiments with carbon monoxide, Giolitti and Carnevali worked at increased pressures and showed that with carbon monoxide and solid carbon the thickness of the case increased considerably when the pressure on the gas was increased from one to over nine atmospheres. Giolitti also studied the action of carbon on iron in the absence of all gases except nitrogen. He concluded that the presence of pure nitrogen did not increase, except to a minimum extent, the carburizing action of the free carbon. Giolitti's work on the direct action of carbon has already been cited above. The findings and reasonings of Giolitti and investigators of the same time proved to be the basis for subsequent theories and researches on pack carburizing as outlined in the following pages.

In ordinary pack carburizing the iron or steel to be case hardened is packed in a carbonaceous material and heated to a temperature of 900° to 950° C. In order to understand the mechanism of this carburization, consider that the pack consists of only pure solid carbon. As the temperature is

increased to around 950° C., the air entrapped in the carburizing box combines with carbon and an atmosphere of nitrogen, carbon monoxide, and carbon dioxide is formed. The carbon monoxide reacts with the steel as shown by the following equation :

$$3Fe + 2CO = Fe_3C + CO_2 \qquad (I)$$

It may be considered that the cementite (Fe_3C) thus formed at the surface of the steel dissolves and thus diffuses inward. There is some controversy among investigators as to the manner in which carbon enters the surface of the steel. Giolitti (1, pp. 358-390), Mahin (5), and Shephard (30) contend that the carbon monoxide diffuses into the steel and gives up its carbon according to the reaction $2CO = CO_2 + C$, but do not offer experimental proof for their statements other than the increased pressure work of Giolitti and Carnvali cited above. Fishel and Woodell (31) reported a rather extensive investigation in which they determined that carbon monoxide can not penetrate iron or steel to an extent capable of accounting for carburization. The researches of Takahashi (32) on this question seem to prove that the reaction is confined to the surface of the steel, although he did not believe in equation (I). His theory is that the carbon is deposited in a finely divided form on the surface and then diffuses into the interior (33). In any event, the carbon monoxide carries the carbon to or into the steel with the formation of carbon dioxide. This carbon dioxide is then

said to react with the hot carbon according to the following equation:

$$CO_2 + C = 2CO \qquad (II)$$

The carbon monoxide then reacts with the steel again. Usually the explanation of the mechanism by which the carbon dioxide is removed from the steel surface and the carbon monoxide again gets back to the surface of the steel is dismissed from the discussion of the above reactions. Ragatz and Kowalke (2) gave a scheme whereby they explained the mechanism in terms of concentration gradients and diffusion of the two gases according to Fick's law. McQuaid (34) suggested that, since carbon in the form of soot, lamp black,or graphite does not carburize iron, the explanation lies in the apparent property of the charcoal to absorb carbon dioxide more strongly than carbon monoxide at red heat. He also pointed out that in order to carburize with carbon monoxide alone it is necessary to have turbulence by a rapid flow of the gas. It is assumed that this is to keep the carbon dioxide from collecting at the surface of the steel. McQuaid believes that the evolution of the carbon monoxide from the charcoal may create the turbulence which aids in the removal of the carbon dioxide from the surface. Since McQuaid has no actual data to show the relative absorbing properties of charcoal for carbon monoxide and carbon dioxide at carburizing temperatures, his theory has met with a great deal of

criticism as evidenced by the discussions at the end of his paper.

Reaction (II) is reversible and therefore involves equilibrium conditions. Much work has been done on the equilibrium gas compositions for the system ($C:CO_2:CO$) represented by this reaction (35, 36, 37). When considering reaction (I), another equilibrium for the system, $steel:CO:CO_2$ is involved. Values for this equilibrium have been determined (38, 39, 40). In regards to the above equilibrium values, Ragatz and Kowalke (2, p. 344) stated: "these values do not necessarily give the gaseous compositions at the gas:carbon and the gas:steel interfaces, as it is always questionable whether the equilibrium values are assumed at the interfaces in a heterogeneous chemical reaction, particularly if one phase is a solid and the other a gas. At the steel:gas interface an additional complication arises due to the constantly varying carbon content of the austenite, which demands constantly changing gas compositions for equilibrium". Granted that the above statements are true, the various equilibrium values determined are nevertheless very helpful in predicting, in a qualitative way at least, what the conditions are inside the carburizing box.

The discussion above has considered only what happens at the surface of the steel. Since the interior of the piece is low in carbon, diffusion takes place and the carbon

migrates from the surface towards the interior. As a result of this diffusion there is a gradual decrease in the carbon content of the case as the core of the piece is approached. This diffusion should follow the ordinary laws of diffusion and the reasoning that goes with Ficks law should apply. The depth of penetration should depend upon the time, the temperature, and the concentration gradient. It has been shown that this is true. Even though the concentration gradient is an important factor in the rate of diffusion, the effect of time or temperature has a more sensitive control over the rate of penetration. This has been brought out by Day (41) and Takahashi (42). Curves showing the variation of carbon concentration with case depth and the relation of case depth to time and temperature have been determined (41, 43, 9). Although the quantitative application of Fick's law to the diffusion of carbon in iron is difficult, there have been some interesting experiments carried out to determine the diffusion coefficients at various temperatures (41, 44). There is much yet to be learned about the diffusion of carbon in iron and, as pointed out by Mehl (45), the field from the standpoint of physical chemistry is almost untouched.

As previously stated, it was known in early times that the addition of certain substances to the charcoal greatly increased the carburizing process, and a knowledge of their existance gave rise to some theories of carburization. These

substances have come to be known as energizers, and the mixture of charcoal and energizer as a carburizing compound. A great deal of work has been done on the mechanism of energizer action since the time of Caron and several theories have been postulated.

One of the first theories of energizer action was the cyanide theory of Caron (24), which has been mentioned in connection with the early developments of carburizing. Giolitti (1, pp. 116-125) stated that it was impossible for him, or other investigators at his time, to detect the presence of cyanides. This is still the case today and the cyanide theory has definitely been abandoned.

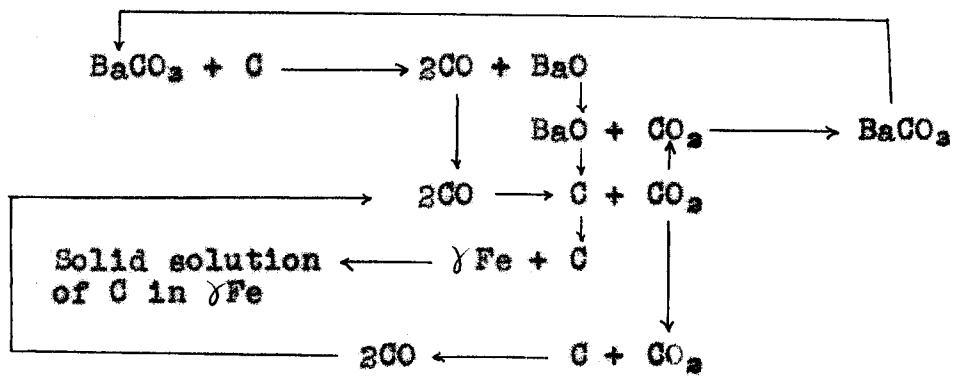
Since the most commonly employed energizers are carbonates, one of the first theories (and still accepted by many, for example, 5, 6) of energizer action was the simple carbon dioxide evolution theory (46, 47, 48, 49). According to this theory, the carbonate dissociates into the metallic oxide and the carbon dioxide at the carburizing temperature. The carbon dioxide then reacts according to equation (2) above and thus increases the amount of carburization. This theory indicates that the efficiency of an energizer would depend upon its ability to liberate carbon dioxide at or just below the carburizing temperature. It has been mentioned above that compounds other than carbonates were known to act as energizers. They, however, were not tested in a

systematic and precise manner. The carbon dioxide evolution theory became inadequate when Fechtchenko-Tchopovsky (50) tested very carefully the action of compounds other than carbonates and found that they definitely exhibited an energizing action. Rodman (51) was one of the first investigators to show that there is no relationship between the energizing power of a carbonate and the quantity of carbon dioxide available. He did not seem to stress the fact that the carbon dioxide should be available at the carburizing temperature and not at a lower temperature.

As discussed below, Takahashi (33) reported experiments which point to the inadequacy of this theory. Ragatz and Kowalke (52) tested the energizing action of a large number of compounds and found that chemicals other than carbonates gave good results. Enos (4) also tested several compounds other than carbonates, although to no extent the number investigated by Ragatz and Kowalke. The results of investigations like these led to the postulation of other theories.

Fetschenko-Tschopiwiskij (53) suggested a theory to explain the energizing action of barium and potassium carbonates. In his theory he suggested a series of cyclic reactions in which the energizer plays an important role. His theory has not met with much comment but it does seem that some of his proposed reactions warrant more investigation. According to his proposed theory the reaction mechanism for

the barium carbonate energizing action is represented by the following scheme:



In 1928 Takahashi (33) carried out a very extensive series of investigations on almost all phases of carbonate energizers. He showed that a carbonate increased the carburization velocity even when there was no dissociation, and that when carburization was carried out in a current of carbon monoxide, the presence of the carbonate accelerated the velocity of carburization even in the absence of solid carbon. Takahashi next showed that when carbon monoxide was passed over heated carbonate, a dense deposit of finely divided carbon was obtained. From these experiments he formulated his theory of energizer action which is essentially as follows; At the carburizing temperature, the carbonate begins to dissociate according to the reaction $MCO_3 = MO + CO_2$ and, with the carbon of the pack, the equilibrium gas composition for the reaction $C + CO_2 = 2CO$ is established. The carbon monoxide then reacts according to the reaction $MO + 2CO = MCO_3 + C$ and the carbon, liberated in a finely divided form,

reacts directly with the steel. The cycle is then repeated. The main criticisms of his theory seem to be that the carbonates which act as energizers do not undergo direct decomposition, as required by his theory, at carburizing temperatures. Also he obtained the deposit of carbon when he passed carbon monoxide over calcium carbonate, which is known to be inert as an energizer.

Another theory of energizers is that proposed by Ragatz and Kowalke (2, p. 347). The statement of their theory is: "the energizing action exerted by certain chemicals in the carburization of steel is primarily due to the catalytic effect produced upon the $C:CO_2:CO$ reaction". They explained the energizing action of the various types of compounds investigated by them (52) on the basis of their theory. According to their theory, the function of barium carbonate as an energizer is as follows: At the point of contact with the carbon, the reaction $BaCO_3 + C = BaO + 2CO$ is said to take place. This direct interaction of carbon with the carbonate increases the carbon monoxide concentration in the main mass of the gaseous phase beyond that demanded by the $C:CO_2:CO$ equilibrium. The partial pressure of carbon dioxide in equilibrium with barium oxide is known to be low. Therefore, they postulate that the absorption of carbon dioxide from the gaseous phase will be more rapid than if the carbon dioxide is required to combine with the carbon. This absorption will lower the carbon dioxide concentration at the steel:gas

interface, and thus there will be increased carburization. Ragatz and Kowalke explain that calcium carbonate and magnesium carbonate are poor energizers because they decompose at too low a temperature and the high partial pressures of the oxides at carburizing temperatures eliminate the possibility of the carbon dioxide absorption pointed out in the case of barium carbonate. They also explain the action of other compounds, such as the cyanides, oxalates, chromates, etc., by stating that the oxides are formed which then react in the same manner as indicated in the explanation of barium carbonate. The theory proposed by Ragatz and Kowalke is very general and tends to explain the action of more types of energizers than any given before. It is the first one postulated (except the cyanide theory) that attempts to explain the energizing action of compounds other than carbonates. The only type of criticism of the above theory that has appeared in the literature is that it calls for experimental investigation.

Enos (4, p. 48) indicated that: "their (only those energizers which can be readily decomposed to yield oxygen) sole role is to produce oxygen-carbon or oxygen-iron compounds". As he pointed out, any definite conclusion from his experiments may be premature.

In the above theories of pack carburization and energizer action there has been no mention made as to the effect of water vapor. In the fields of gas carburizing and

furnace atmospheres a great deal of work has been done on the effect of water vapor, for example, pure dry nitrogen is inert but in the presence of very small amounts of water vapor it becomes very actively decarburizing. As has been pointed out in the Introduction, there is some controversy among metallurgists concerning the effect of small amounts of water vapor in ordinary pack carburization. Unless extreme precautions are taken, there will always be at least small amounts of water vapor present in the materials used for pack carburizing, and the question of the effect of these small amounts of water vapor on ordinary pack carburizing seems important.

The mechanism of the steam-carbon reaction has recently been reviewed by Scott (54). As he points out, there is some doubt as to what reactions occur, and especially there is doubt as to the primary reaction. Most data, however, indicate that below 1000° C. the primary reaction is $C + 2H_2O = CO_2 + 2H_2$. Other reactions which probably occur are: $C + H_2O = CO + H_2$ and $CO + H_2O = CO_2 + H_2$. Since hydrogen is one of the products in all of these reactions, and carbon dioxide in all but one, it might be thought that the presence of water vapor would always have a decarburizing action. As pointed out in the Introduction, Webber (10) used the reaction $C + 2H_2O = CO_2 + 2H_2$ to explain the increased decarburization obtained when he used soaked charcoal at 800°C. It seems a little remote that small amounts of water vapor would give

enough of the decarburizing gases, especially hydrogen, to have a very pronounced decarburizing action.

It might be that traces of water vapor would have a catalytic effect (either positive or negative) on some of the reactions listed in the above theories of energizers. Also there is the possibility that the reaction between the carbon and water may have an effect on the surface of the charcoal to make it show selective absorption for carbon dioxide or carbon monoxide.

Because of the controversy among metallurgists as to the effect of water vapor, the omission of it in the energizer theories, and the possibilities of its effect mentioned above, the moisture investigations reported in this thesis were performed.

III. EXPERIMENTAL

A. Apparatus

A schematic diagram of the apparatus used in this investigation is shown in Figure I. Part of the winding of the electric resistance furnace (H) was a helix coil of No. 8 Chromel "A" wire. This coil, of thirty turns, had an outside diameter of 6.25 cm. and was 30 cm. long. It was mounted inside an alundum tube which had a wall thickness of 1 cm. In addition to this coil, there were four turns, 1 cm. apart, around the outside of each end of the alundum tube. These were for the purpose of maintaining a more nearly uniform temperature over the entire length of the furnace. The assembly was insulated by means of Silocel contained in the furnace shell (Q). By carefully probing the vitreosil furnace tube (I) with a thermocouple, it was found that there was a 7.5 cm. region over which the temperature did not vary by more than 0.5° C. The center of this uniform temperature region of the furnace will be designated as "thermal center". The vitreosil thermocouple sheath (J) was arranged so that the thermocuople junction was always on thermal center. A chromel-alumel thermocouple was used, the junction being made by welding the two ends together in the flame of a carbon arc. Not more than three runs were made without

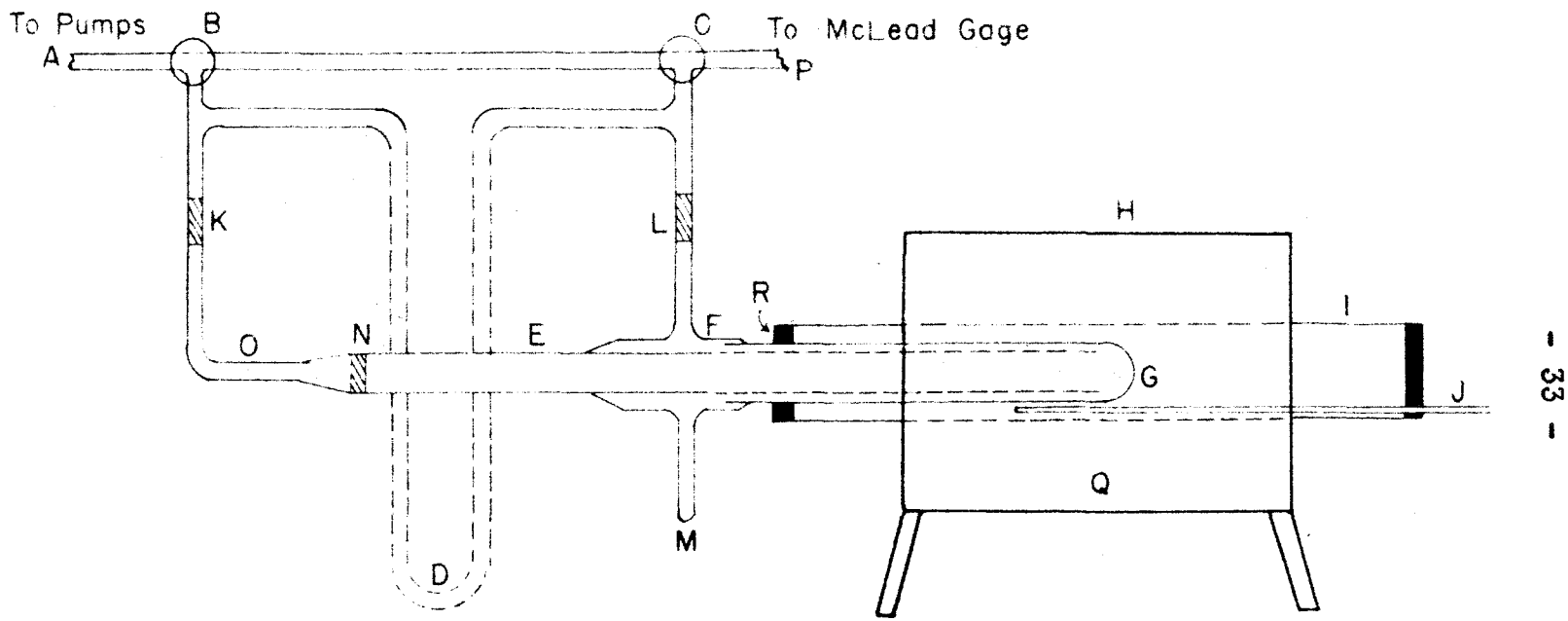


Figure I, Schematic Diagram of Apparatus

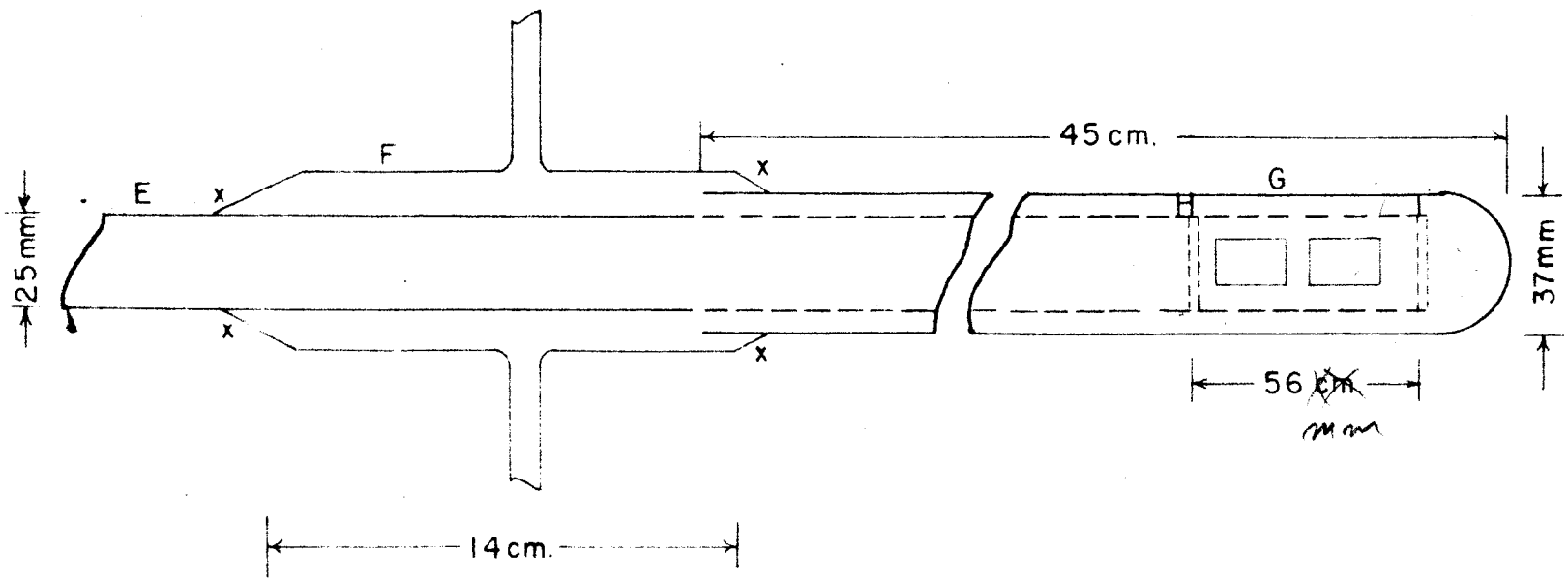


Figure II. Detailed Diagram of Tube and Sample Assembly.

renewing the junction. The thermocouple wires were checked against chromel and alumel wires obtained from the Bureau of Standards. All temperatures were controlled to within ±3° C. by means of a Leeds Northrup recording controller. The temperatures listed in this work are the average values as controlled by the regulator. The vitreosil tube (G) was 45 cm. long, had an inside diameter of 44 mm., a wall thickness of 3 mm., and was closed at one end. It was held in place by means of the rubber ring (R). Inside this tube was placed another vitreosil tube (E). This tube was 75 cm. long, had an inside diameter of 23 mm., and a wall thickness of 2 mm. The pack and samples were placed in (E) as described in the Method of Procedure. The pyrex sleeve (F) was sealed to the tubes (E) and (G) by means of Pyseal at the points marked X in Figure II. In Figure I Pyseal was used to make the pyrex to pyrex seals (K) and (L) and the pyrex to vitreosil junction (N). The differential mercury manometer (D) served to show the difference in pressure across the pack. The three-way stop cocks (B) and (C) connected the assembly to the vacuum line. At (A) was connected a mercury-vapor pump with a Megavac force pump. A mercury manometer was connected to the discharge side of the vapor pump. The McLeod gage was at point P.

It was necessary in part of this investigation to pass air through the pack by admitting air at (M) (Figure I). In order to maintain a small difference in pressure between (A)

and (M), the set-up shown in the following figure was used in place of the Megavac oil pump.

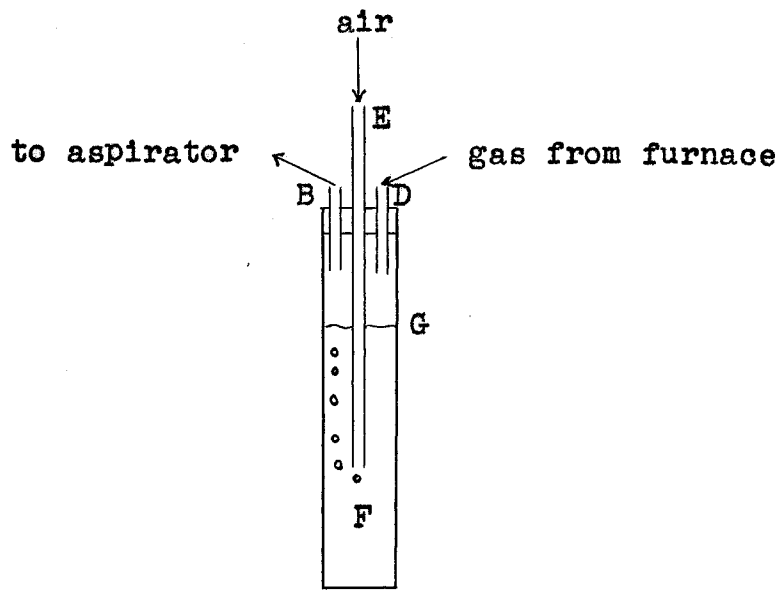


Figure III. Pressure Regulator

The glass tube (F) contained water to a level (G). A water aspirator was connected at point (B) and connection to (A) (Figure I) was made at point (D). By varying the distance which the open tube (E) extended below the surface of the water, it was possible to maintain different pressures in the space above the water.

Two gas trains were required for the moisture investigations; one for drying air and one for obtaining air saturated with water vapor at the temperature of the room. The first unit of the drying train was a gas washing bottle containing saturated sodium hydroxide. This was followed by

a drying tube (30 cm. long and 30 mm. inside diameter) packed with a 9 cm. layer of anhydrous calcium chloride and a 16 cm. section of Drierite. The two drying agents were separated by a layer of cotton and were packed so as to fill the entire cross section of the tube. This train could be connected through a stopcock to (M) in Figure I. The train used to saturate the air with water vapor consisted of two gas washing bottles; the first containing saturated sodium hydroxide and the second distilled water. This train could also be connected through a stop cock to (M) in Figure I. In both cases the seals at (M) were made with Pyseal. The saturated sodium hydroxide wash was used to remove any CO_2 from the air and as a means for determining the rate of gas flow through the pack.

B. Materials

1. Sugar Charcoal

The sugar charcoal used in this investigation was prepared from C.P. dextrose which had an almost negligible ash content and contained no sulfates, chlorides, aluminum, calcium or heavy metals. The sugar was first reduced to a charred mass by heating in porcelain casseroles. The charred material was then placed in a steel can which had a depth of 30 cm. and a diameter of 15 cm. This container was closed by welding on a steel cover which was provided with a

vacuum connection. The container was then placed in a Hump furnace, connection made to a water aspirator and the pressure reduced to 2 cm. before the heating was started. As the temperature increased, the pressure gradually increased due to the further decomposition of the charred sugar, and at about 500° C. a large amount of liquid (mostly water) was evolved. The temperature was controlled at 645° C. for two hours, during which time the pressure dropped to 2 cm. Upon raising the temperature to 700°C. the pressure increased to 7 cm. with a further but small amount of liquid being evolved. The temperature was controlled at 700°C. for three hours, during which time a pressure of 5 mm. was obtained by means of the Megavac oil pump. The furnace was then turned off and the pressure kept reduced until room temperature was reached. The lid of the container was removed on a lathe and the sugar charcoal placed in a tightly covered bottle. Thirty five gram portions were ground in a porcelain mortar and placed in the closed end of the vitreosil tube (G) in Figure I. The tube was then placed in the furnace so that the section containing the charcoal was in the uniform temperature region of the furnace.

A special adapter, not shown in the figure, was used to connect tube (G) directly to the vacuum line (A). The pressure was reduced to less than 50 microns and the heating started. The temperature was controlled at 950° C. for two

hours and then raised and controlled at 1000° C. for an additional two hours. The pressure at the time the furnace was turned off was about 50 microns and on cooling to room temperature, the pressure dropped to less than one micron. The treated charcoal was stored in a dessicator until used. The yield of treated charcoal was 13 o/o of the weight of the sugar taken. The ash in the prepared charcoal was found to be 0.23 o/o. The ash was insoluble in hot dilute HCl. A sieve analysis of the charcoal used in all runs was as follows:

+ 30 mesh	15.9 o/o
+ 60 mesh	19.0
+ 80 mesh	13.0
+100 mesh	10.4
+200 mesh	20.7
-200 mesh	21.0

2. Steel

The steel used throughout the quantitative part of the work reported here was obtained in the form of 3/8", cold-drawn squares and had the following analysis:

Carbon	0.173 o/o
Manganese	0.750
Phosphorus	0.020
Sulphur.	0.027
Silicon.	0.173

A spectrographic analysis of the steel showed also traces of copper, germanium, chromium, and tin. The steel exhibited

a normal case after carburizing. Figure IV is a photomicrograph of the steel as received.

Figure IV. Photomicrograph of Original Steel. X 50
Etched in Nital

3. Carburizing Compound

The carburizing compound used in this investigation contained 15 o/o by weight of barium carbonate which was of reagent grade and met the specifications of the American Chemical Society. The sugar carbon was the same as described above. In making up the compound the charcoal and barium carbonate were mixed by grinding them together in a mortar. After grinding, the compound was placed in a tightly covered bottle and rolled to insure thorough mixing. The carburizing compound was kept in a dessicator until used.

C. Method of Procedure

The steel samples used throughout the investigations were 19 mm. in length and 9 mm. on each side. They were obtained from the above 3/8" cold-drawn squares. The samples were reduced to size by grinding equally the sides and ends on a No. 30 Oxaluma wheel. (Identification marks were stamped on the ends of the samples.) During the grinding operation, the samples were held with a clean cloth in order to avoid contamination of the surfaces with grease from the hands. The specimens were handled at all times with bone-tipped tweezers. After grinding, the samples were washed in absolute alcohol and in redistilled ether. They were transferred directly from the ether to a dessicator and allowed to come to room temperature before being weighed. All specimens weighed approximately 13 grams and did not vary in weight by more than 13 mg.

The specimens were packed in the tube (E) as indicated in Figure II, the perforated plates (H) and (I) being used to keep the pack in place. Charcoal was placed on plate (H) to a depth of 6 mm. One of the samples was placed on this layer and packed by tamping charcoal tightly around it. This was followed by another 6 mm. layer before the second sample was packed and the plate (I) placed in position.

The tube containing the packed samples was placed inside tube (G) and the assembly connected to the vacuum line as shown in Figure I. All connections were made with Pyseal.

The entire length of the pack was located in the uniform temperature region of the furnace. New charcoal was used for each run.

For the various reduced pressure runs down to 2 mm. a five liter flask, provided with an air inlet, was placed between the Megavac pump and the vacuum line. By varying the amount of air bled into the flask while the pump was operating, the various desired pressures could be maintained. The purpose of the flask was to eliminate the fluctuations in pressure due to the cycle of the pump. The pressure in the system was first reduced to a low value in order to test for leaks with a spark coil. Air was then let in and the "bleeder" adjusted to maintain the desired pressure. The furnace was turned on and when temperature was reached, which was 950° C. for all the variable pressure runs, the recording controller was set. The average time for the furnace to reach this temperature was 1 hour and 35 minutes. The number of hours at temperature signifies the time interval between the time the temperature was reached and the time the current was turned off. The average rate of cooling from 950° C. to 600° C. was approximately 4 °/minute as the samples were furnace cooled to room temperature under the pressure of the run. The assembly was then disconnected and the samples removed. They were washed thoroughly in ether, placed in the dessicator, and weighed after they had reached the temperature of the room. After sawing off 3 mm. from one end of

the sample, the sawed surface of the remainder of the sample was polished and etched for microscopic examination.

In making the "vacuum" runs, the samples were prepared and packed as explained above. The pressure in the system was kept reduced during these runs by means of the continuous operation of the Megavac and mercury-vapor pumps, the flask and "bleeder" being disconnected from the line. A spark coil was used to test for leaks in the system. Heating was started after the pressure was reduced to less than 19 microns. In Figure V are given representative time-temperature curves along with the corresponding time-pressure curves for a number of carburizing runs. Points A, B, C, D, and E show the times at which the temperatures 1000°, 950°, 900°, 850°, and 800° C. respectively were reached, while the points A', B', C', D', and E' on the pressure curves show the pressures at the times these corresponding temperatures were attained. Since the rate of heating and the change in pressure with temperature was approximately the same for all runs up to the lowest temperature under consideration (800°), the portion of the time-pressure curve FME' is common to all of the runs and is independent of the temperatures reached. After the desired temperature was reached and the controller set, the pressure dropped as shown by the curves.

As an example, consider the curve (F M B' B" N) for the 950° run. At room temperature the pressure was 19 microns. Thirty minutes after turning on the current, and at a

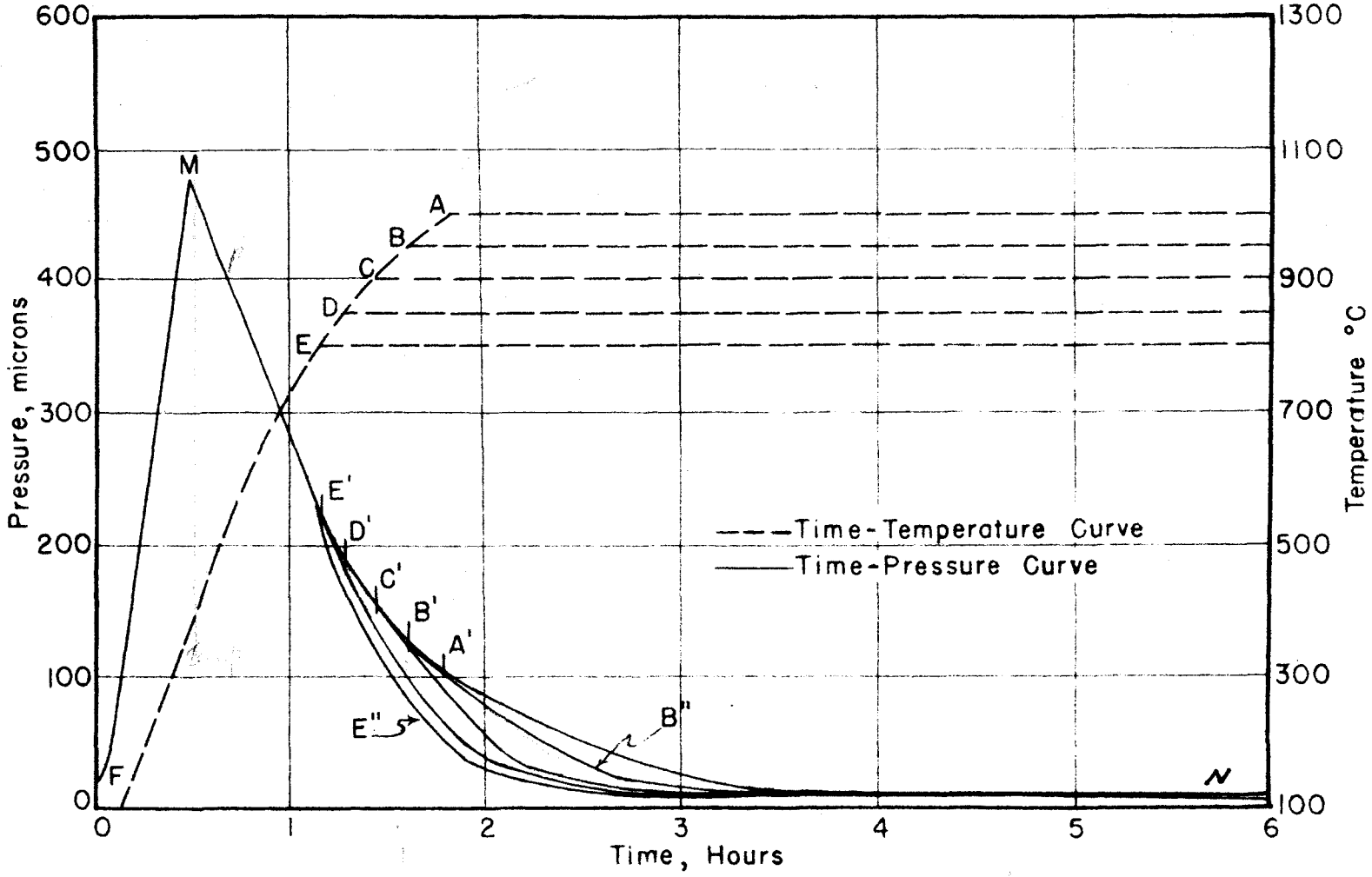


Figure V. Typical Time-temperature and Time-pressure Curves for the Low Pressure Determinations.

temperature of 380°, the pressure had increased to 475 microns (M). It then decreased rapidly until at 950° and a time of 1 hour and 35 minutes the pressure was 125 microns (B'). One hour later the pressure had decreased to 25 microns (B") and after four hours at temperature, when the current was turned off, the pressure was 14 microns (N). Similarly the remaining time-pressure curves represent the conditions for the other temperatures, for example, the curve (F M E' E" N) is for the 800° run. Upon cooling to room temperature, the pressure decreased, for example, at 630° the reading on the McLeod gage was 0.10 micron. The change in pressure during the cooling period is not shown by the curves in Figure V. After the furnace had reached room temperature and air was let into the system, the samples were handled as outlined in the procedure for the variable pressure runs.

The same procedure as given above was followed for the 950° "vacuum" runs in which the time at temperature was varied. The "zero" time at temperature samples were run in the same way, the current being turned off as soon as temperature was reached. As shown by the curve (F M B' B" N) in Figure V, the pressure at the end of the 1 hour and 10 minute run was 30 microns. In the case of the 8 hour and the 16 hour runs the pressures at the time the current was turned off were 10 microns and 5 microns respectively.

The investigations using dry air and air saturated with

water vapor at room temperature involved the use of procedures quite different from those given above. Consider first the runs using a non-energized pack. The gas trains used to obtain the dry air and the saturated air are described under the Apparatus. All samples were prepared and packed in the same manner as previously described. One of the trains was connected to tube (M) (Figure I) through a stopcock. With the stopcock closed, the pressure in the system was reduced to about 50 microns by means of the Megavac pump. The pump was then turned off and air allowed to bubble through the train into the system. This flushing operation was carried out three times. The pressure was then reduced by means of both the Megavac and mercury-vapor pumps. When the pressure had been reduced to 19 microns or less the heating was started, the pressure varying with time and temperature in the same manner as shown in Figure V. When the desired temperature was reached, the stopcock (B) (Figure I) was turned so as to close the system to the vacuum line (A). The stopcock between (M) and the train was then opened and air allowed to pass into the system at the rate of approximately 1.5 ml. per minute. While the system was filling with air the pressure apparatus shown in Figure III was connected to (A). When the system had reached atmospheric pressure, stopcock (B) was opened and stopcock (C) was turned so as to require the air entering at (M) to pass through the pack. The rate of flow

was adjusted to one bubble or approximately 0.3 ml. per minute. The differential on the manometer (D) was about 5 mm. At the end of the four hour period at temperature the current was turned off and the air flow continued until room temperature was reached. The samples were then handled in the same manner as in other runs. The only difference in procedure between the runs involving dry air and air saturated with water vapor at room temperature was the gas trains used.

The samples for the runs in which the carburizing compound was used were prepared in the same way as described above. They were also packed the same except that the compound was used in place of the sugar charcoal alone. The same gas trains were employed for this part of the investigation as were used for the non-energized moisture investigations. After the seals were made, the pressure in the system was reduced to approximately 0.1 mm. and the air let back in through the gas train at the rate of 1.5 ml. per minute. When all the air was in, the pressure was reduced and the air again allowed to enter through the gas train. This flushing operation was repeated three times after which the pressure regulator (Figure III) was connected at (A) (Figure I). The stopcocks (B) and (C) were adjusted so that the air passed through the pack. The flow of air was then adjusted to about 1.5 ml. per minute, this rate of flow being maintained for approximately nine hours. When the heating was started, the flow of air through the system was reduced to 0.3 ml. per

minute. A 5 mm. differential was shown by the manometer (D). The temperature was controlled at the desired temperature for four hours, after which the furnace was allowed to cool to room temperature without interrupting the flow of air. The samples were handled in the same manner as in other runs. Again the only difference in the procedures for the runs involving dry air and air saturated with water vapor at room temperature was the gas train used.

The preliminary polishing of each sample was carried out by polishing from a No. 30 Oxaluma wheel through numbers 150, 1, 2-0, 3-0, and 4-0 emery papers respectively. The final polishing was done using levigated alumina suspended in a soap solution which contained glycerine. Care was taken to keep the edges of the samples as square as possible. The etching was for 7 seconds in 5 o/o Nital. The samples were then examined under the microscope at 100 diameters. After selecting a representative sample for a given set of conditions, a representative side was picked for photographing. In order to obtain as sharp an edge as possible, the chosen sides of two samples were clamped together and the complete polishing procedure repeated. The etching time for the samples to be photographed varied from 8 seconds for hypoeutectoid cases to 18 seconds for hypereutectoid cases.

The photomicrographs were taken at a magnification of 50 diameters on a Leitz metallograph. The source of light

was a direct current carbon arc which was operated at 4 amperes on 110 volts. A plate of Noviol "C" and a plate of Sextant green were used as filters. Eastman contrast orthochromatic antihalation film was used for all photomicrographs. The exposure time varied from 1 second to 4 seconds, the time depending upon the sample being taken. The film was developed for 5 minutes at 18° C. in Eastman D-19 developer, and fixed for 7 minutes in Eastman F-5 fixer. Azo F-4 paper was used for making the prints.

In measuring representative case depths, three values were determined: total case depth (depth to the core), depth of the hypereutectoid zone, and depth of the eutectoid zone (the hypereutectoid plus euctectoid region). Measurements were made at 50 diameters on the ground glass slide of the metallograph and check measurements were made on the photomicrographs. All measurements were checked by an independent observer.

IV. PRESENTATION AND DISCUSSION OF RESULTS

A. Low Pressure or "Vacuum" Carburization

The procedures used to obtain the data presented below have been given in the Method of Procedure. Each figure for weight increase is an average value obtained from data of at least two determinations.

1. The Effect of Pressure on Carburization

For this part of the investigation the pressure in the system was varied from atmospheric to the "vacuum" pressures. The temperature was 950° C. and the time at this temperature was four hours. The data obtained on this phase of the work are given in Table I. The curve showing the variation of the weight increase with pressure is given in Figure VI. Here the gain in weight is plotted against the pressure in milimeters on semilogarithmic paper. Photomicrographs of representative cases for each sample are given in Figure VII. They are arranged in the same order as in Table I.

The curve in Figure VI indicates that as the pressure in the system was decreased from atmospheric the carburizing action (or gain in weight) showed a slight but general increase until a pressure of about 12 mm. was reached. As is evident from the irregularities in the weight increase

Table I

Data Showing the Effect of Pressure on Carburization
Temperature, 950° C., Time, 4 hours at temperature

Photomicrograph (See Fig. VII)	Pressure (mm.)	Average Weight Increase (mg.)	Type of Case	Representative Depth of Case (mm.) Hyper.	Eutectoid	Total
A	739.0	12.5	Hypo.	-	-	1.00
B	369.0	17.5	Hypo.	-	-	1.00
C	186.0	15.8	Hypo.	-	-	1.00
D	44.0	25.1	Hypo.	-	-	1.06
E	16.4	23.5	Hypo.	-	-	1.04
F	12.0	42.0	Eutectoid	-	0.60	1.20
G	9.0	46.7	Hyper.	0.38	0.72	1.30
H	5.5	52.8	Hyper.	0.60	0.86	1.36
I	3.0	50.8	Hyper.	0.50	0.80	1.25
J	2.0	52.8	Hyper.	0.60	0.90	1.40
K	"vacuum"	51.1	Hyper.	0.52	0.82	1.36

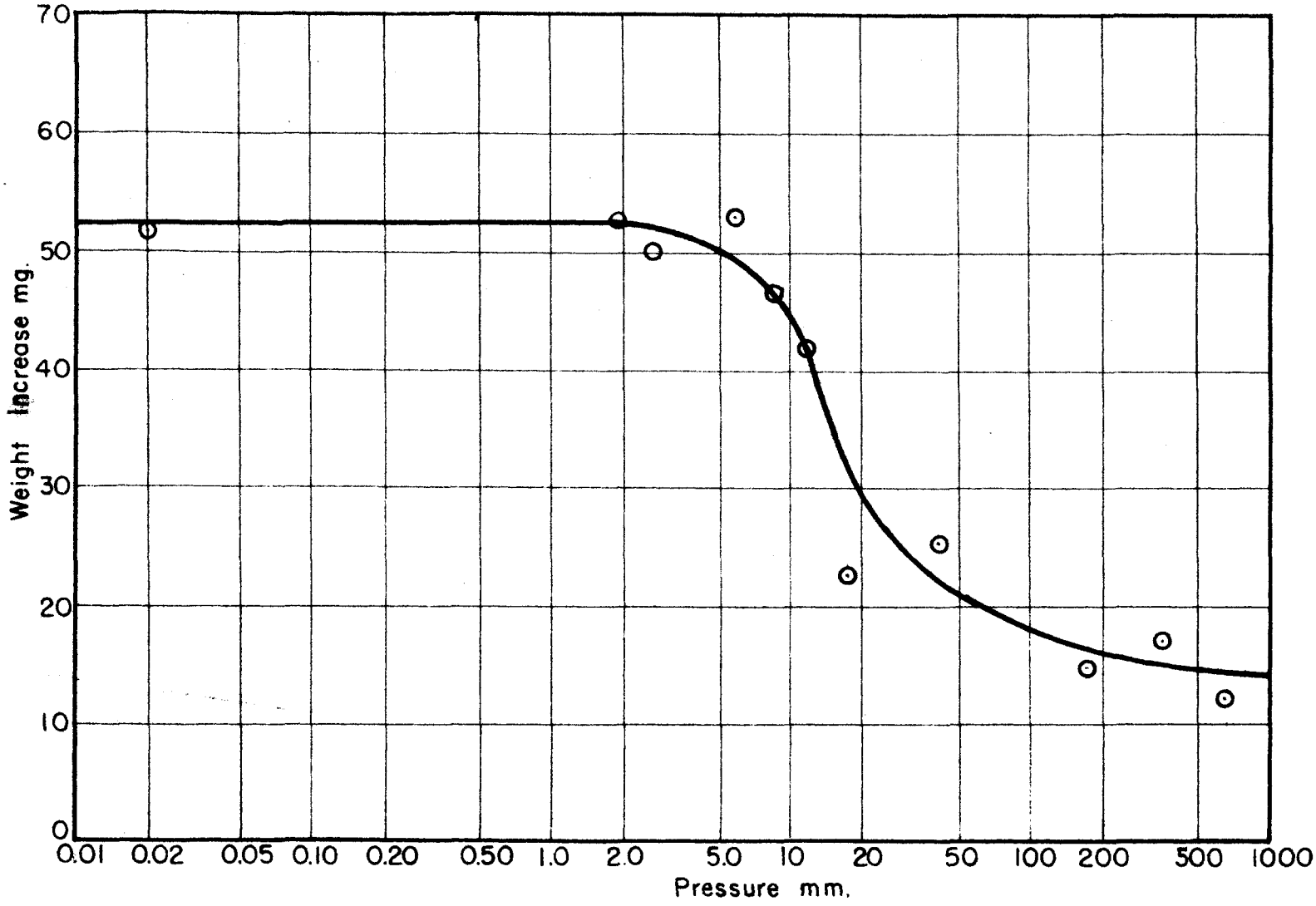


Figure VI. Curve Showing the Effect of Pressure on the Increase in Weight. Temperature, 950° C. Time, 4 hours at temperature.

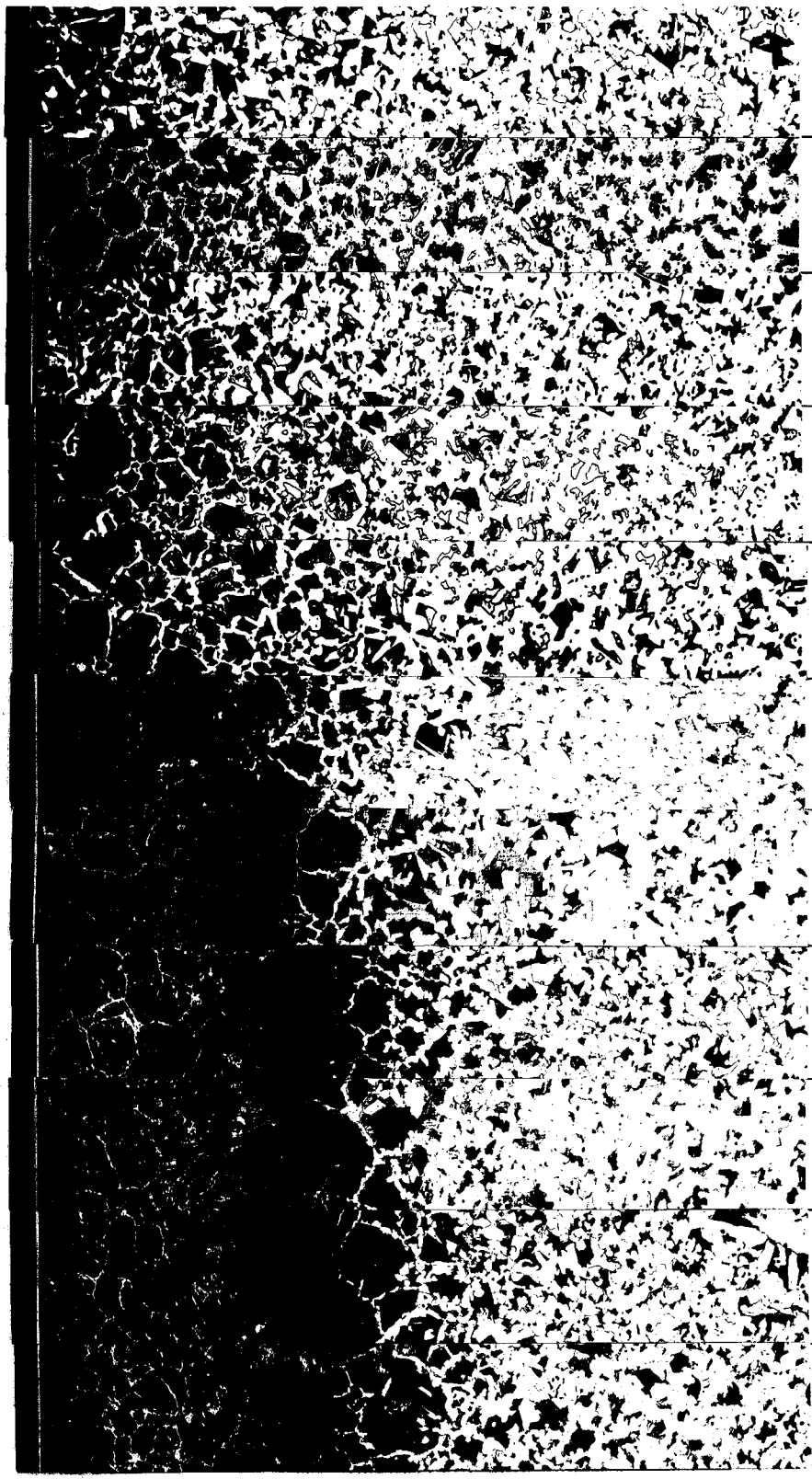


Figure VII. Effect of Pressure on Carburization. 950°C. 4 Hours at Temp. Surface of Sample Indicated by White Line at Left, X 50

data, the carburization was somewhat uneven in the range from atmospheric pressure to a pressure of about 12 mm. The samples showed temper colors and small spots where apparently the action had been less. With the small cases obtained at these pressures it was difficult to ascertain the actual effect of these spots because, possibly due to diffusion, the cases appeared fairly uniform. This is shown by the photomicrographs (A), (B), (C), (D), and (E) in Figure VII. The cases, however, vary slightly in appearance from sample to sample, but the total case depths of the five samples are very nearly the same. The results at atmospheric pressure (A) show that the carburizing capacity of the charcoal is very small under the usual conditions of pressure. Enos (4) ran some determinations using sugar charcoal alone at atmospheric pressure and obtained slight carburization. Although he used a temperature of 915° C. and time of 6 hours, the results obtained by him are comparable to those reported here; both showing the slight carburizing capacity of sugar charcoal in unenergized pack carburizing.

At a pressure of 12 mm. the gain in weight almost doubled in comparison to that obtained at 16.4 mm. The photomicrograph (F) shows the difference in the case produced. The appearance of the surface of the samples was also different, there being fewer spots and less temper color than at the higher pressures. From 12 mm. to 5.5 mm. there was only

a gradual change in the amount of carburization and the change, if any, from 5.5 mm. to the "vacuum" pressures was negligible. The samples (H), (I), (J), and (K) showed practically no spots and the cases obtained were uniform. As shown by the photomicrographs of these samples, the cases were normal and contained well defined zones of hypereutectoid, eutectoid, and hypoeutectoid. The structure of a typical hypereutectoid zone (J), as brought out by an alkaline sodium picrate etch, is shown in Figure VIII. By comparing the weight increase data with the photomicrographs it can be seen that there is good correlation between the amount of carbon in the case and the gain in weight.

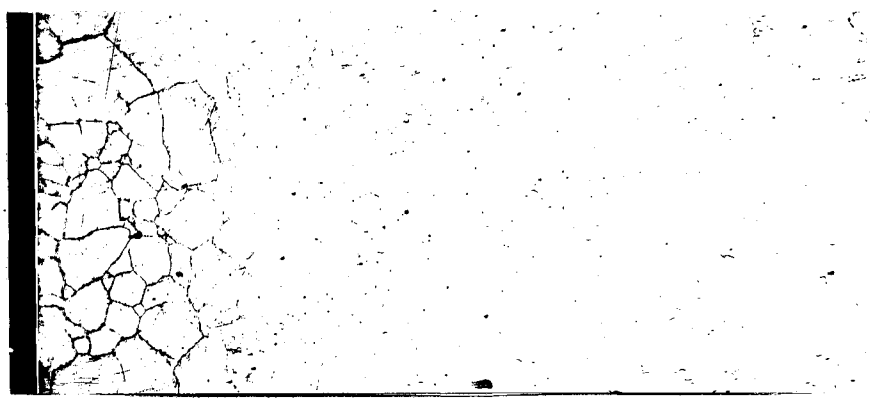


Figure VIII. Photomicrograph of Sample (J) Figure VII Alkaline Sodium Picrate Etch. X 50

From a study of Figure VI and the case depth data of Table I it is evident that the total case depths for all the

samples are nearly the same, the great differences being in the carbon content of the case. This indicates that there is a difference in the diffusion rate with relation to the concentration gradient for the carburization which takes place at the higher pressures and that which takes place at the lower pressures. According to the laws of diffusion, it does not seem that the penetration at the higher pressures would be as comparable to those at the lower pressures since the amount of carbon entering, and thus the concentration gradient, is so much different. One possible factor to be considered in the explanation of this effect is that at the higher pressures a gas within the metal effects the diffusion of the carbon.

Giolitti (1, pp. 358 - 390) has reported the results of experiments in which he carburized with carbon monoxide and solid carbon at pressures above atmospheric. By increasing the pressure on the gas from one to nine atmospheres he increased the carbon concentration in the case and almost doubled the depth of penetration. According to Giolitti, these results indicated that the carbon monoxide penetrated the steel and deposited carbon. It can also be argued that the increase in pressure increased the carbon deposition at the surface of the steel and the increased penetration was due to the increased carbon gradient. The mechanism of the method of carbon deposition is of course a debateable question. The results of the penetration in

relation to carbon content obtained at atmospheric and the lower pressures might, however, point to the action of some gas in aiding penetration, yet being practically inert as far as its ability to deposit carbon. This gas could either penetrate into the iron at the carburizing temperatures or already be present in the iron. As the pressure is diminished at the elevated temperatures, this gas would then be reduced at the surface and in the interior and its effect on the carbon penetration would be greatly reduced. At these diminished pressures, the carbon enters the surface of the steel to a much greater extent and diffusion takes place due to the concentration gradient created. Perhaps the gas which is postulated to aid in this carbon penetration is nitrogen, hydrogen, or oxygen. Nothing has appeared in the literature relative to the effect of these gases on the penetration of carbon, and as pointed out by Grossmann (7), there is much yet to be learned about their effect during carburization. The gas might also be carbon monoxide, but again the effect of this gas in the metal is not known and as to whether it diffuses into the steel during carburization is unknown. The explanation given above is only in the form of an hypothesis and suggests the need of considerable experimental verification.

The "vacuum" sample (K) shows that carburization was obtained when very low pressures were used. The curves

showing the variation in pressure with time and temperature during the running of a sample similar to (K) have been given and explained in the Method of Procedure (Figure V). In review, during these "vacuum" runs the pressure increased from 19 microns at 25° C. to about 475 microns at a temperature of 380° C. It then decreased so that by the time 950° C. was reached the pressure was 125 microns. The pressure continued to decrease and at the end of four hours at 950° C. was 14 microns. The question arose as to when did the carburization occur and does it continue after the pressure has been reduced to a very low value? In order to study this, the "vacuum" carburizations were carried out for different periods of time at 950°C.

2. The Effect of Time

The data for this part of the investigation are given in Table II.

Figure IX shows the weight increase as a function of time at temperature and Figure X shows the case depth versus time at temperature. Photomicrographs of representative cases for the various times are given in Figure XI. They are arranged and labeled in a manner corresponding to that of Table II.

Table II

Data Showing the Effect of Time at Temperature on Carburization
Temperature, 950° C. Pressure, "vacuum".

Photomicrograph (See Fig. XI)	Time at 950° C.	Average Weight Increase (mg.)	Type of Case	Representative Depth of Case. (mm.) Hyper.	Eutectoid	Total
A	0	1.0	Hypo.	-	-	0.04
B	1 hr. 10 min.	27.5	Eutectoid	-	0.44	0.88
C	4 hrs.	51.1	Hyper.	0.52	0.82	1.36
D	8 hrs.	63.8	Hyper.	0.64	1.10	2.04
E	16 hrs.	83.8	Hyper.	0.82	1.60	2.90

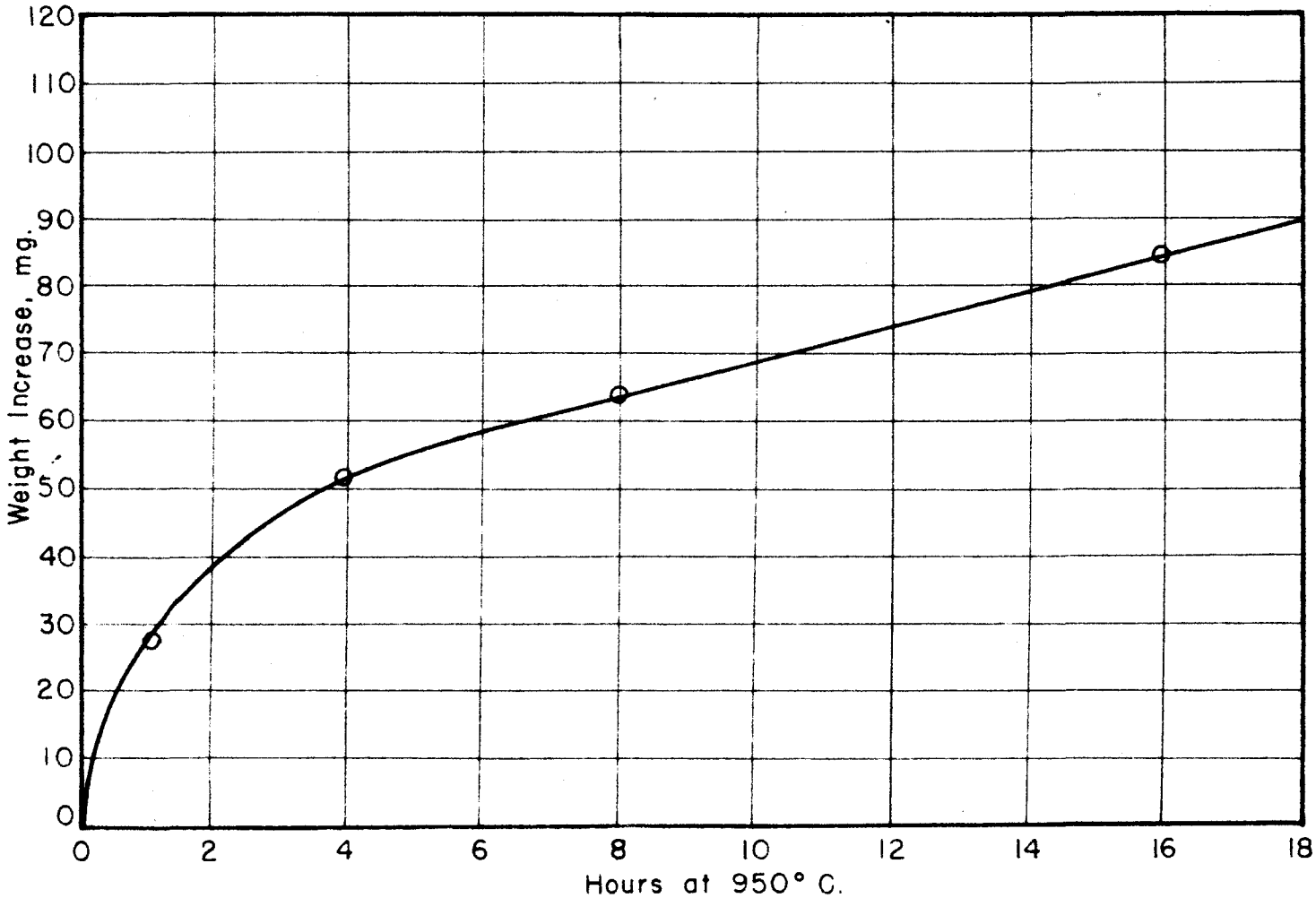


Figure IX. Curve Showing the Effect of Time at Temperature on the Increase in Weight. Temp. 950° C. Pressure, "vacuum".

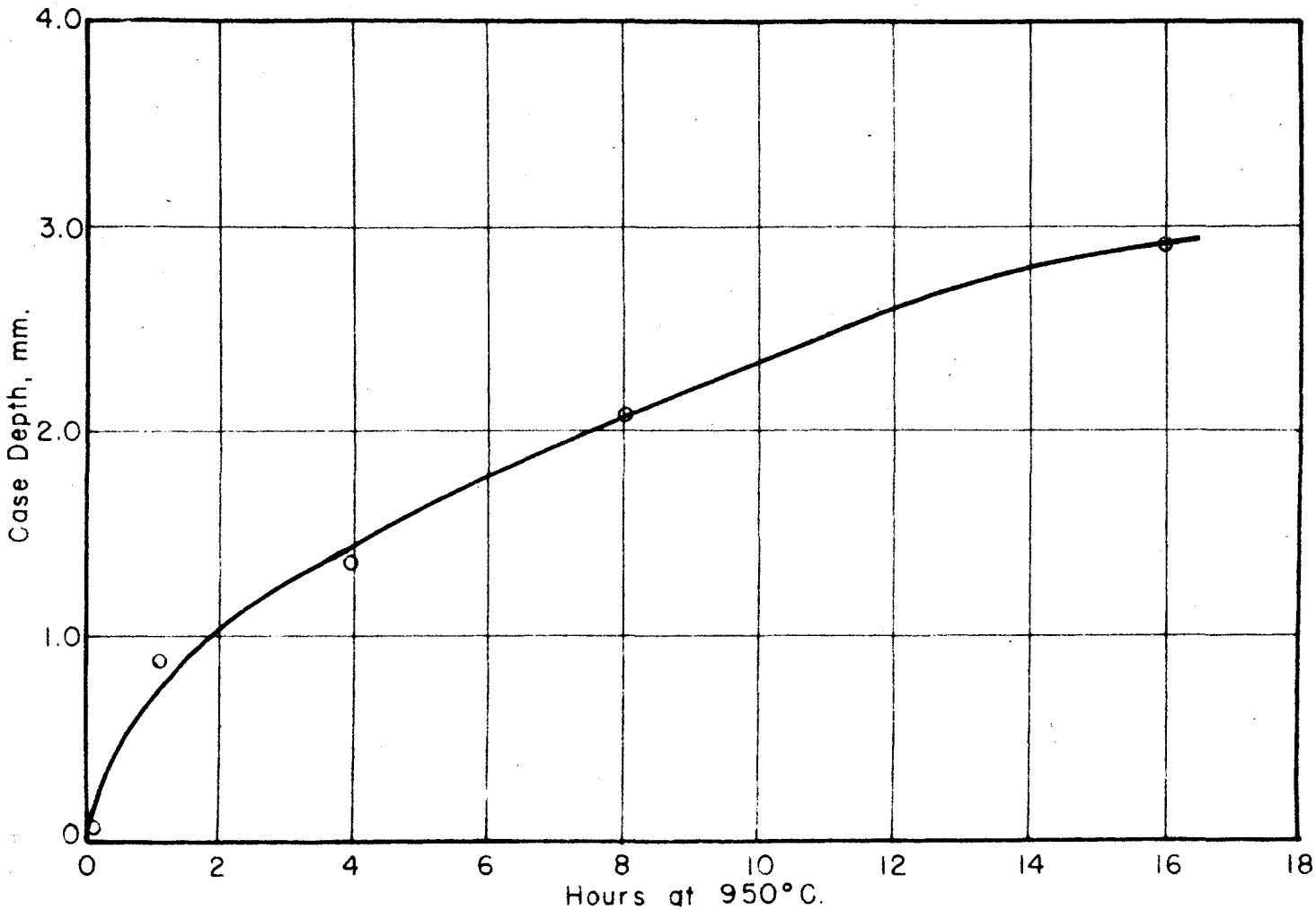


Figure X. Time at Temperature-penetration Curve. Temp. 950° C. Pressure, "vacuum".

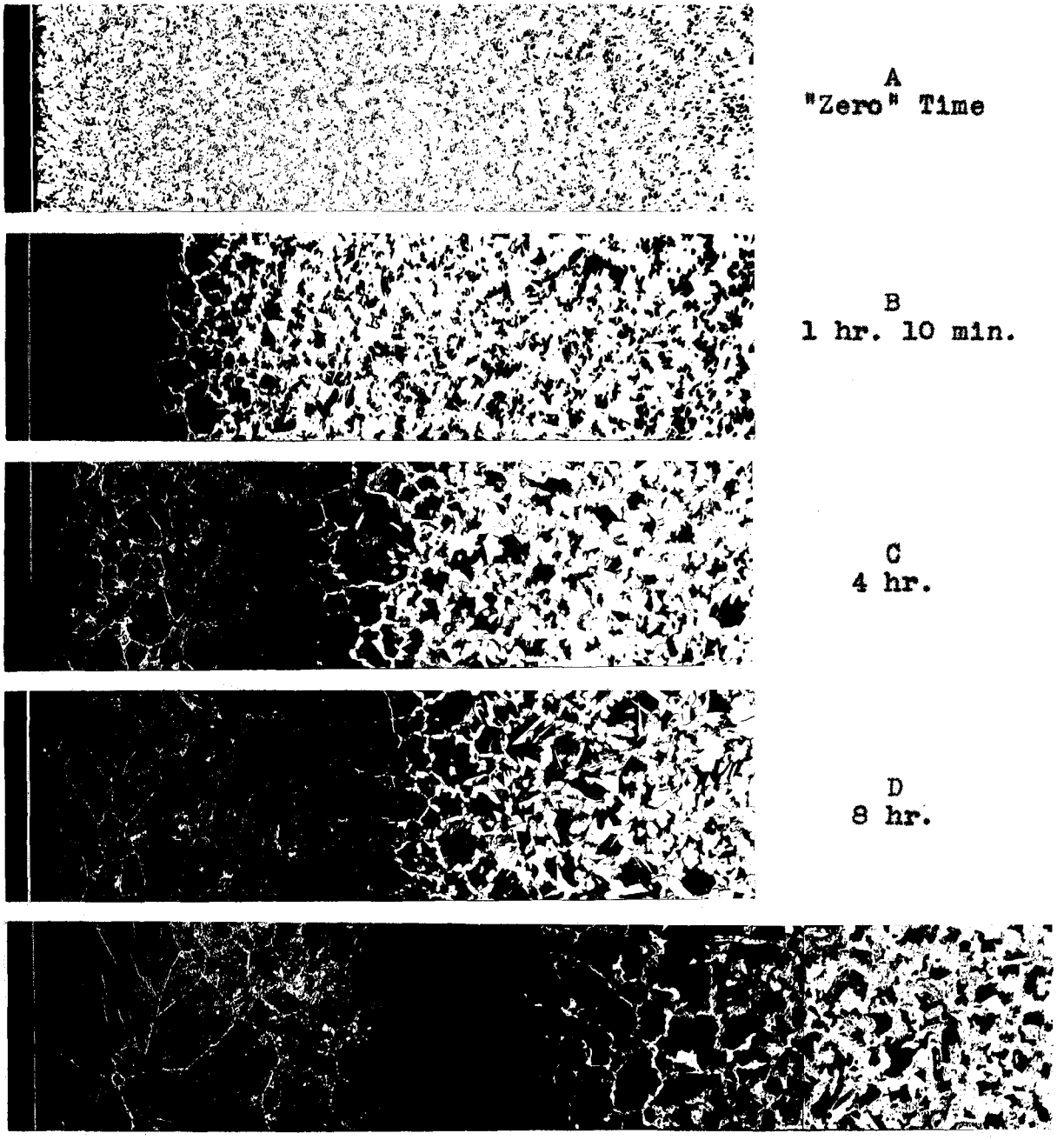


Figure XI. Effect of Time at Temperature on Carburization. 950°C. Pressure, "Vacuum". Surface of Sample Indicated by White Line at Left. X 50

The "zero" time samples were run the same as any other "vacuum" samples except that the heating current was turned off when the temperature reached 950° C. The photomicrograph (A) and the data in Table II indicates that the carburization which took place on heating to temperature and cooling was very slight. The next time at temperature was one hour and ten minutes. This time was chosen because in that interval the pressure dropped from 135 microns to a pressure (20 microns) which was close to that maintained for the remainder of a four hour run. The results of the time are given in the table and figures already referred to in the Discussion. The four hour, eight hour, and sixteen hour samples show that there was a definite increase in the amount of carburization with time at a pressure of only a few microns. Figure IX indicates that carburization would continue beyond the sixteen hour period. The time, however, was not extended beyond sixteen hours because, due to the coalescence of the cases of adjacent sides, further carburization would no longer have been representative. In Figure XII is given a photomicrograph of samples (B), (C), (D), and (E). This shows, more or less visually, the effect of time on the case obtained and also points out that the size of the sample limits the time of representative carburization to sixteen hours. All photomicrographs of cases shown at 50 diameters were made from sections near the middle of the sides of the square sections shown in Figure XII. The pressure for the eight

hour run varied the same as for the four hour run and continued to decrease after this time, for example, after four hours at temperature the pressure was about 14 microns, an hour later 11 microns, and at the end of the eight hour period it was 10 microns. The pressure also varied in approximately the same way for the sixteen hour run; the pressure at the end of eight hours being 8 microns, at the end of 12 hours 7 microns, and at the end of sixteen hours 5 microns. The curve showing case depth versus time (Figure X) is typical of time-penetration curves given in the literature (42) for other methods of carburizing. The data obtained from the time at temperature lead to the following facts concerning the "vacuum" carburization:

1. Very slight carburization occurs during the heating and cooling period used in these experiments.
2. The amount of carburization increases with time.
3. Carburization takes place at very low pressures (5 - 10 microns), as is shown especially by the eight hour and sixteen hour runs.
4. The higher pressure of the gas which was produced on bringing the system up to 950° C. (see Figure V) was not effectively carburizing.

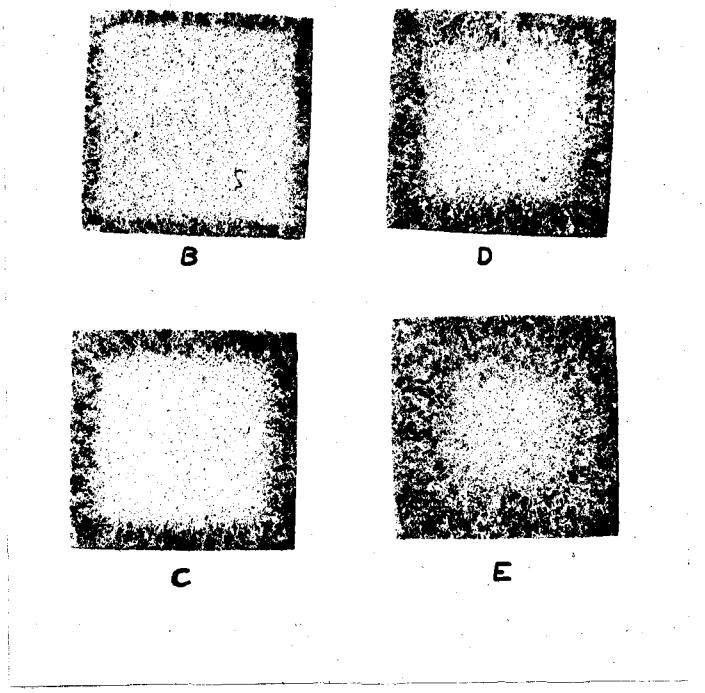


Figure XII. Photomicrograph of Samples (B), (C), (D), and (E). (Figure XI) X 3

3. The Effect of Temperature

The effect of temperature on the "vacuum" carburization was studied by running samples at 800°, 850°, 900°, 950°, and 1000° C. The time at temperature was four hours in all determinations. The data obtained are given in Table III.

Table III

Data Showing the Effect of Temperature on Carburization
Time, 4 hours at temperature, Pressure, "vacuum"

Photomicrograph (See Fig. XV)	Temp. (° C)	Average Weight Increase (mg.)	Type of Case	Representative Depth of Case. (mm.)		
				Hyper.	Eutectoid	Total
A	800	2.1	Hypo.	-	-	0.14
B	850	6.8	Hypo.	-	-	0.48
C	900	19.5	Eutectoid	-	0.26	0.80
D	950	51.1	Hyper.	0.52	0.82	1.36
E	1000	74.5	Hyper.	0.78	1.20	1.85

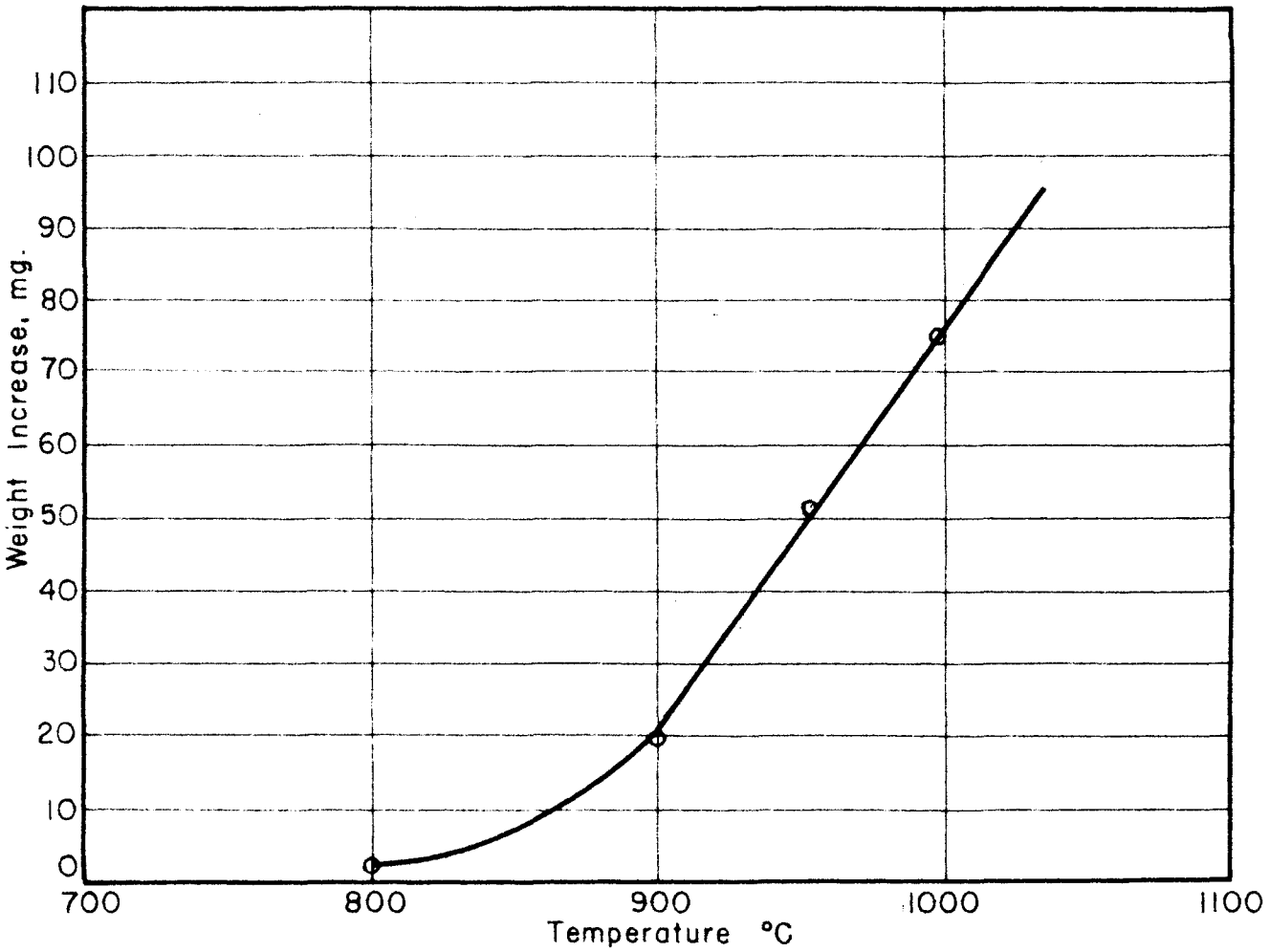


Figure XIII. Curve Showing the Effect of Temperature on the Increase in Weight. Time, 4 Hours at Temp. Pressure, "Vacuum".

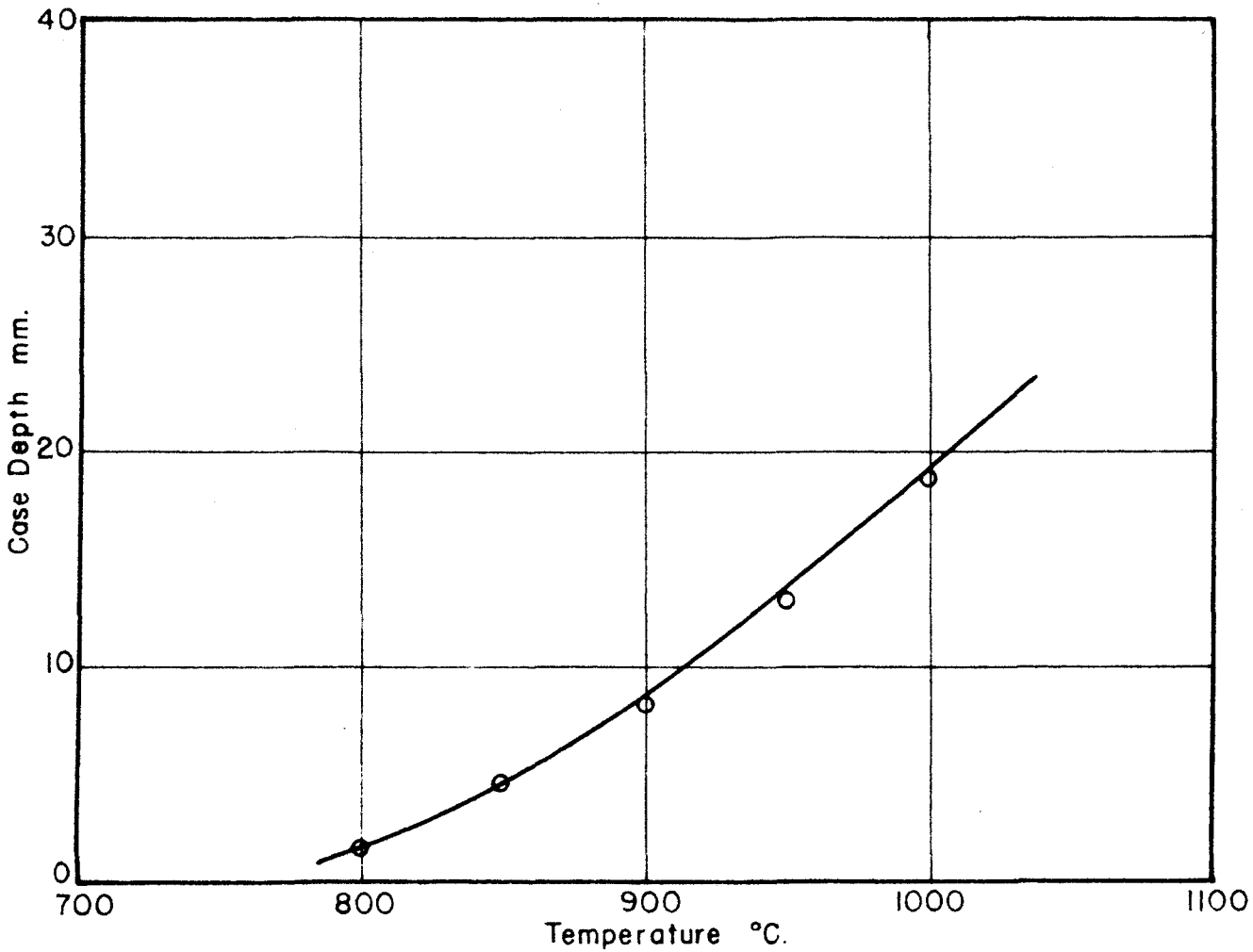


Figure XIV. Temperature-penetration Curve.
4 Hours at Temp. Pressure, "vacuum".

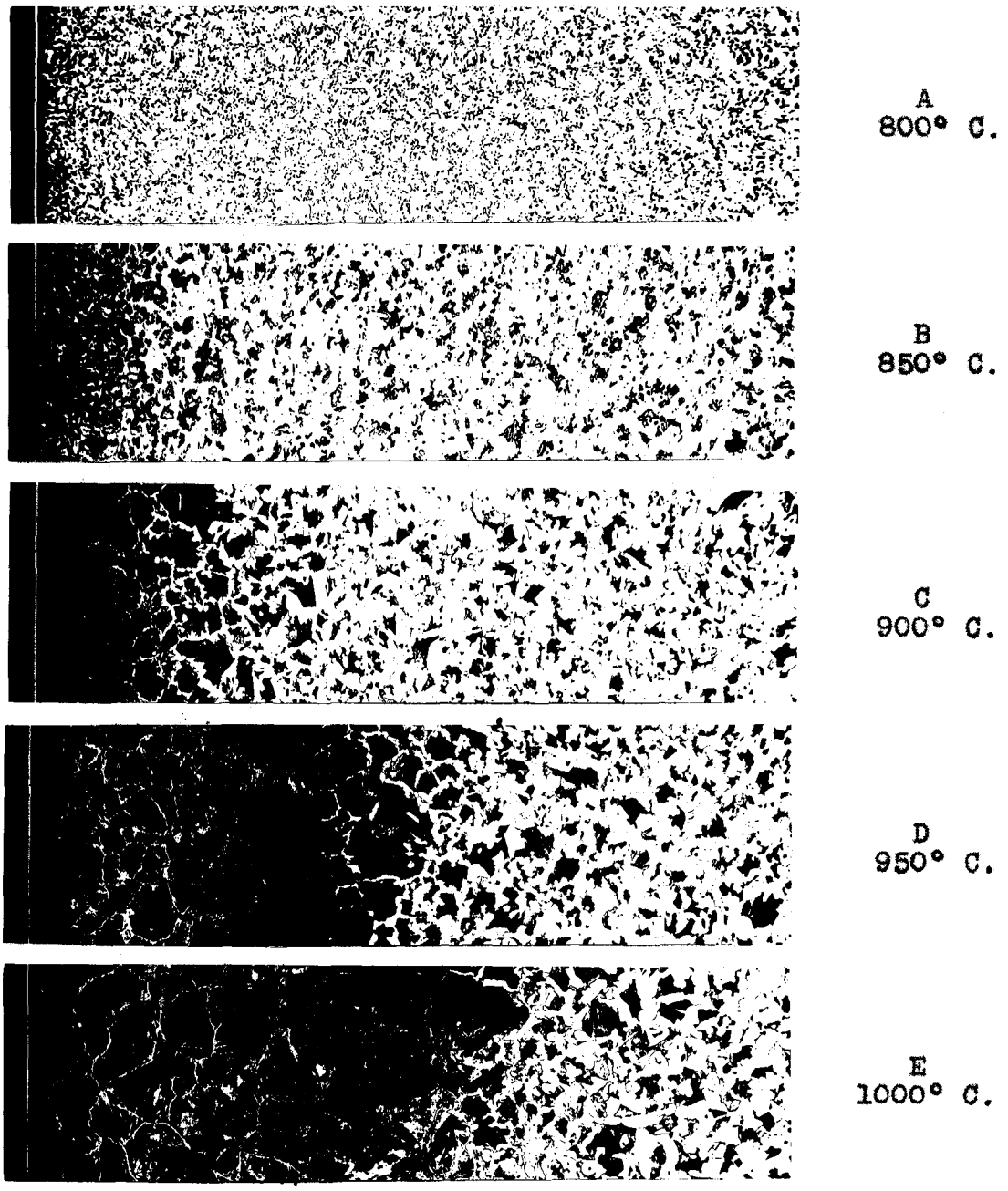


Figure XV. Effect of Temperature on Carburization. 4 Hours at Temp. Pressure, "Vacuum". Surface of Sample Indicated by White Line at Left. X 50

Curves showing the weight increase as a function of temperature and the variation of case depth with temperature are given in Figures XIII and XIV respectively. Photomicrographs of the representative cases obtained are given in Figure XV. The weight increase-temperature curve (Figure XIII) shows that carburization was increased considerably by raising the temperature. The case depth-penetration curve in Figure XIV is typical of similar curves given in the literature (9) for ordinary pack carburizing. It can be concluded from this phase of the investigation that the carburization at the low pressure follows the same general trends with respect to temperature as would be expected from the laws of rate of reaction and diffusion.

4. General Discussion

The results given above show that carburization was obtained at very low pressures and that the carburization at these pressures followed the same general trends with respect to time and temperature as does ordinary pack carburizing. In order to arrive at the experimental conditions used for the "vacuum" or low pressure runs, several investigations were carried out to overcome experimental difficulties and to study the general characteristics of the process.

One of the first experimental difficulties encountered was uneven carburization, that is, there were small spots on the surface of the samples which proved to be points at which

the carbon penetration was less. This type of carburization had to be eliminated before the weight increase data could be used in making correlations. Investigations on the preparation of the proper surface led to some interesting facts. It was found that if the surface of the cold-rolled steel was washed well, but not ground down, that the carburization did not take place. Experiments were carried out to determine the effect of various degrees of surface polishing. The outer surface was always removed on the No. 30 Oxaluma grinding wheel as described in the Method of Procedure. (It had previously been found that the grinding of the surface to a greater depth made no difference.) The surfaces were then polished on papers ranging from 1 grit through 4-0 paper. Some surfaces were polished with levigated alumina after finishing through the 4-0 paper. The results obtained indicated that the carbon penetration was the same whether the surface was ground on the Oxaluma wheel or first on this and then polished on finer papers. It was also found that the carburization was uneven if a paper or fine grinding wheel left a film or discoloration which did not wash off in the alcohol or ether. Since the degree of polishing had no effect on the results, it was found best to use the Oxaluma wheel and thus avoid the possibility of the film and discoloration difficulties given above.

While experimenting with the uneven carburization, it

was thought that perhaps the spots could be eliminated by applying something to the surface which would assure very close contact of the carbon. The surfaces were ground down on the grinding wheel and a thin film of pure vaseline applied. Fine charcoal was sprinkled over this film and the samples packed in the usual manner. The carburization was found to be very slight and the surfaces showed many spots, which upon microscopic examination of the case, indicated practically no carbon penetration. Other samples were dipped in a thin syrup made from the sugar used for the preparation of the charcoal. This covered the surfaces with a very thin but even film of syrup. The samples thus prepared were packed and run in the usual manner; the results being comparable to those obtained when nothing was applied to the ground surfaces. The investigations outlined above showed that the surfaces must be freshly ground and clean. To obtain these conditions, the method of sample preparation outlined in the Method of Procedure was adapted. Even when this procedure was used, the cases sometimes were spotted with low carburized areas which evidently had not had sufficient contact with the solid pack.

Another experiment in connection with the "vacuum" carburization was to treat the samples for four hours at 950° C. under the reduced pressure without the pack. The pressure at the beginning of this type of run was reduced to a value of about 1 micron. During the heating, the

pressure increased to about 10 microns at around 950° C. but soon decreased to the vicinity of 1 micron or less. After cooling under the reduced pressure, the samples showed a slight discoloration and a loss of about 0.10 mg. in weight. Some of the sides of these samples were then reground on the Oxaluma wheel while other sides were left as they were after the treatment. The samples were packed and run in the usual manner. The results indicated that the coloration produced by the heating of the samples under the reduced pressure had a slight effect on the carbon penetration. The sides which were reground before carburizing showed more even penetration than the sides which had not been so treated. This again emphasized the necessity of having clean fresh surfaces.

In order to ascertain if the carburization which took place at the low pressures was inherent with the particular set of experimental conditions being used, the investigations given in the following paragraphs were carried out.

A sugar charcoal which had been prepared at least twenty years ago in Germany was used. It was found that this charcoal was in about the same stage of preparation as the charcoal prepared in the porcelain casseroles (see Materials). It therefore had to be given a preliminary treatment under reduced pressure in order to obtain a product which could be run at low pressures. This treatment was carried out in a manner similar to that outlined under Materials. The charcoal was then used for a pack in the regular "vacuum"

procedure. Comparable carburization was found to take place.

As pointed out in the procedure for the preparation of the sugar charcoal, the material which was treated in the Hump furnace was given a final treatment under reduced pressure at 1000° C. This was done in order to obtain a charcoal which gave a minimum pressure increase when used as a pack for the "vacuum" runs. Some runs were made using the prepared sugar charcoal before it was given this final treatment. The pressure with this charcoal increased to around 4 mm. in the vicinity of 800° C. When a temperature of 950° C. was attained, the pressure was about 2.5 mm. and at the end of four hours at temperature it had decreased to 60 microns. The carburization obtained was comparable to that found when using charcoal which had been given the final treatment. Spectrographic carbon rods that had been heated to 2400° C. were ground up and used as a pack. The results were of the same order as those obtained with sugar charcoal.

Runs were also made using Bees-Wax for all the seals in place of Pyseal. No difference in the "vacuum" carburization was found. The vitreosil tubes (G) and (E) (Figure I) were replaced by other vitreosil tubes and again the results of the low pressure carburization were the same. Loosely packed samples in open crucibles gave good carburization in the vacuum at 950° C. Cold-rolled steels of approximately the same carbon content, but from other sources, were run and the results found to be comparable. A hot-rolled steel

and a carbonyl iron were tested in the vacuum pack and the strong carburization effect was again observed.

The experiments cited above show that the "vacuum" or low pressure carburization was quite generally obtainable with pure carbon and ordinary steels; an important factor being the condition of the surface of the steel.

5. Comparison with Previous Investigations

The previous investigations on carburization at low pressures have been reviewed in the History. In most of these the experimental conditions were not given enough in detail to be able to evaluate the results obtained. The experiments of Giolitti (1, pp. 116-134) and those of Weyl (32) were reported more in detail and an interpretation of their work is possible. Both Giolitti and Weyl obtained very slight carburization with sugar charcoal in, what they termed, a vacuum. The pressures used by Giolitti were in the vicinity of 0.5 mm., while those used by Weyl were about 0.2 mm. Both experimenters had an arrangement whereby they could heat the charcoal and the iron under the reduced pressure and then effect contact of the two without changing the pressure. They also flushed the system with nitrogen during the preliminary heating of the iron and the charcoal. The carburization experiments were run at 1000° C. for three hours. As outlined in the History, Guillet and Griffith (21) also ran a series of experiments at reduced pressures

(pressures not listed) and applied pressure to the iron in order to insure intimate contact. They obtained very slight and uneven carburization and then only when the iron was pressed firmly against the charcoal.

In none of the three papers referred to above did the writers report the character of the surface of the samples used. As has been explained, the preparation of the surface was very important. If a clean fresh surface was not used, and especially if the original rolled surface was used, the carburization was very slight or nil. Furthermore, it is possible that the investigators changed the surfaces of their samples during the heating before the iron was brought in contact with the charcoal. Even though Giolitti did not have the iron at the same temperature as the charcoal during the preliminary treatment, a study of the diagram of his apparatus shows that the iron possibly reached a temperature high enough for the surface to be affected by the gases present. Giolitti pointed out that the porcelain tube used was porous at the high temperature, thus limiting the pressure obtained to 0.5 mm. It was reported above that even the slight coloration obtained when the samples were heated alone at pressures as low as 10 microns had a definite interference effect on the "vacuum" carburization.

The pressures used in this investigation were much lower than any previously reported, yet as can be seen from the results, very good carburization was obtained. The very

slight or negative carburizing effect reported by others for vacuum work could have been due to the condition of the surfaces of the steel samples.

B. Moisture Studies

1. Sugar Charcoal Pack

The details of the procedure used for the moisture investigations with the sugar charcoal pack have been given in the Method of Procedure. The runs were carried out in the same manner as the low pressure or "vacuum" runs except that when the desired temperature was reached, either dry air or air saturated with water vapor at 25° C. was let in. The air was then passed through the pack at a rate of 0.3 ml. per minute. The time at temperature was four hours. At least two runs were made for each set of conditions, the weight increase value given being an average figure. The data obtained for sets of samples run at corresponding temperatures, but with different moisture contents in the air, are given in Table IV. Photomicrographs of representative cases obtained at the various conditions are given in Figure XVII. They are arranged and labeled as in Table IV.

Table IV

Data Showing the Effect of Dry Air and Air Saturated with Water Vapor at 25° C. on Carburization with Sugar Charcoal. Time, 4 hours at temperature, Pressure, Atm.

Photomicrograph (See Fig. XVII)	Temp. (°C)	Moisture in air (mm. H_2O)	Average Wt. Increase (mg.)	Type of Case	Representative Depth of Case. (mm.) Hyper.	Eutectoid	Total
A	800	0	-3.4	Decarb.	-	-	-0.36
B	800	25.2	-3.8	Decarb.	-	-	-0.34
C	850	0	0.6	Hypo.	-	-	0.06
D	850	25.2	1.6	Hypo.	-	-	0.14
E	900	0	7.5	Hypo.	-	-	0.43
F	900	25.2	8.2	Hypo.	-	-	0.42
G	950	0	15.2	Hypo.	-	-	1.00
H	950	25.2	16.5	Hypo.	-	-	1.00

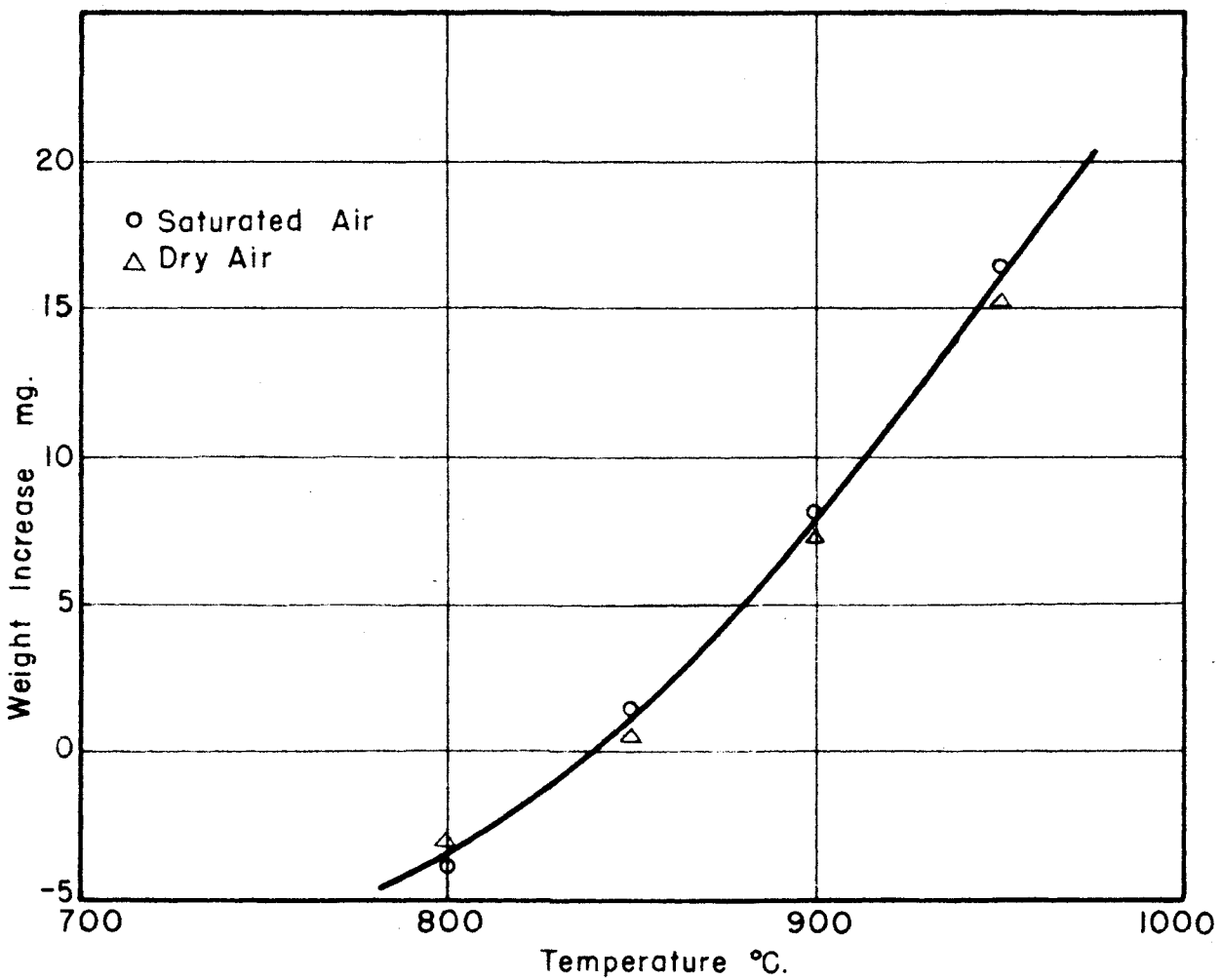


Figure XVI. Curve showing the Effect of Moisture on Carburization at Various Temperatures. 4 Hours at Temp. Charcoal Pack.

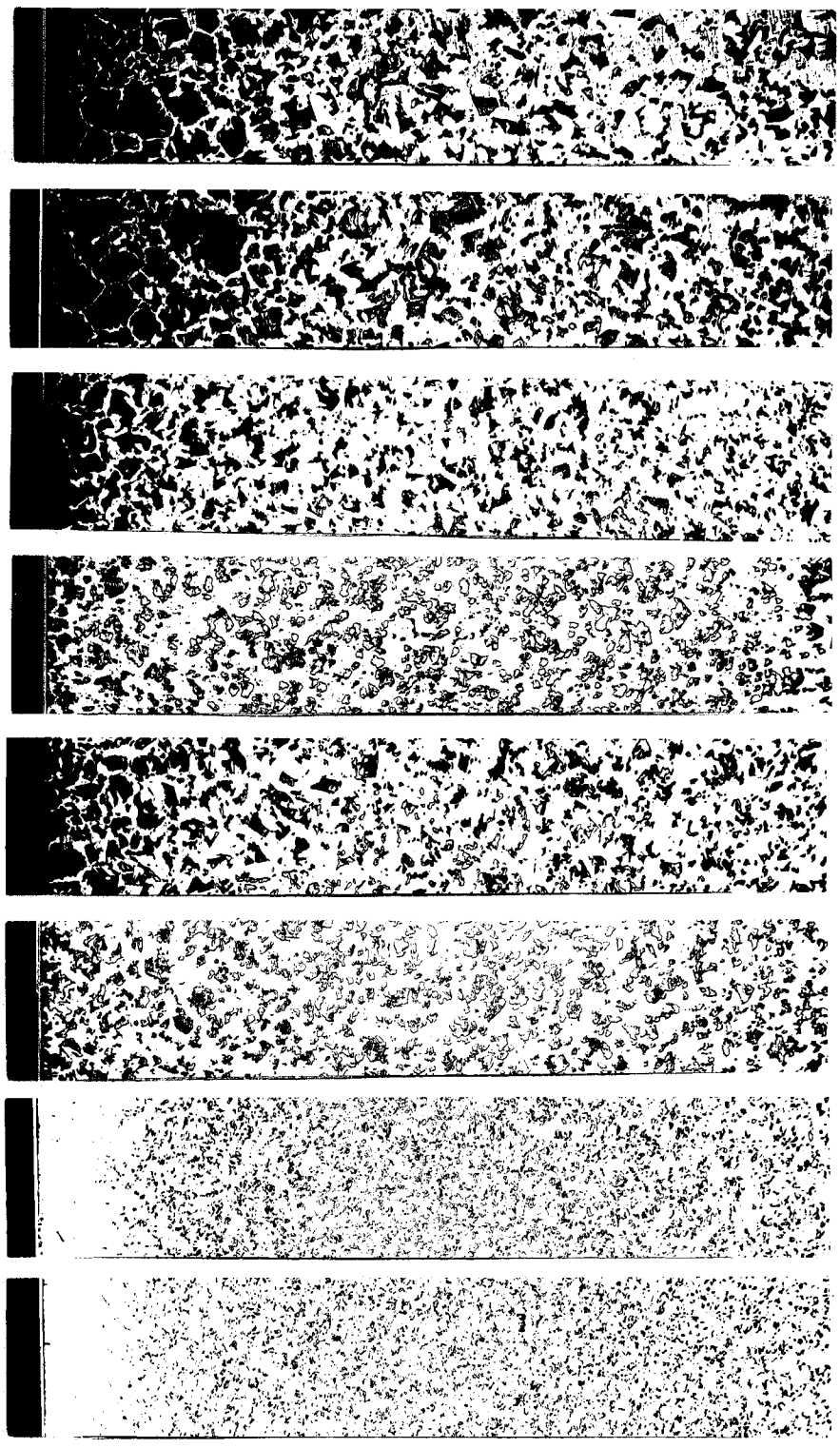


Figure XVII. Effect of 25.2 mm. H_2O Vapor on Carburization 4 Hours at Temp. Pack, Sugar Charcoal. Surface of Sample Indicated by White Line at Left. X 50

The weight increase data show that there is, on the average, a constant difference of about 1 mg. in favor of the samples run with air saturated with water vapor at 25° C. (25.2 mm. H_2O). This is shown graphically in Figure XVI, where both sets of data are plotted. As brought out by the case depth data, the slight difference in weight increase does not effect the carbon penetration. There is, however, a small difference in the appearance of the case obtained at 950° C. (G) and (H) (Figure XVI). Sample (H), which was run with saturated air, has less ferrite extending to the edge of the samples than does (G), which was run with dry air. The same trend is also shown by samples (E) and (F), although not quite as much.

The samples run at 800° C. were decarburized, the amount of decarburization being practically the same with dry air as with saturated air. Decarburization with unenergized charcoal in the vicinity of 800° C. is not uncommon, having been reported by several writers (10, 55, 56, 57, 58). At this temperature the reaction $2CO = CO_2 + C$ shifts to the right, thus giving at equilibrium a high percentage of carbon dioxide in comparison to carbon monoxide. The amount of the decarburizing gas, carbon dioxide, present probably accounts for the decarburization at this temperature. It was pointed out in the Introduction that Webber (10) obtained increased decarburization with wood charcoal at 800° C. by first soaking the charcoal in water and allowing the excess to drain

off. It is obvious that his results are not comparable with those reported here because of the large amount of moisture which he had present. Also, it should be remembered that the atmosphere here was forced through the pack while Webber's experiment probably represents a static condition. The results reported in this thesis, however, seem to contradict Webber's statement that: "extreme care must be taken to remove all moisture from the atmosphere, even in the presence of carbon".

It can be concluded from the series of investigations reported in this section that, under the experimental conditions used, the presence of 25.2 mm. of water vapor has no important effect on carburization with sugar charcoal.

2. Energized Sugar Charcoal Pack

The procedure used for the moisture investigations with a 15 o/o barium carbonate pack has been given in the Method of Procedure. The pressure was not kept reduced until the desired temperature was reached because, if this had been done, the effect of the energizer would not have been representative. The flushing out of the system and the nine hours of passing air through the pack would have provided the desired atmosphere with respect to moisture. The time at temperature was four hours and, again, the weight increase figures are average values obtained from at least two runs. Some fusion of the barium carbonate on the surface of the

samples was noticed at 950° and 875° C. The surfaces were cleaned well with a stiff brush in alcohol and ether, thus removing practically all the fusion product. From the checks obtained it was considered that the weight increase values were reliable for making correlations. Considerable soot or graphite deposition was also noticed. This sort of deposition has recently been reported by Sutton and Ragatz (9).

The data obtained for this phase of the investigations are given in the usual manner in Table V and Figures XVIII and XIX.

The weight increase data indicate that there was again the small difference in favor of the samples run with air saturated with water vapor at 25° C. This is also shown by the curve in Figure XVIII, where both sets of data are plotted. The photomicrographs (Figure XIX) do not show the difference in case structure that was noticeable with the samples run in sugar charcoal alone.

Table V

Data Showing the Effect of Dry Air and Air Saturated with Water Vapor at 25° C. on Carburization with 15 o/o $BaCO_3$ Pack. Time, 4 hours at temperature, Pressure, Atm.

Photomicrograph (See Fig. XVIII)	Temp. (°C)	Moisture in air (mm. H_2O)	Average Wt. Increase (mg.)	Type of Case	Representative Depth of Case. (mm.) Hyper.	Eutectoid	Total
A	800	0	2.3	Hypo.	-	-	0.11
B	800	25.2	3.3	Hypo.	-	-	0.12
C	875	0	25.7	Eutectoid	-	0.36	0.77
D	875	25.2	27.9	Eutectoid	-	0.38	0.80
E	950	0	54.0	Hyper.	0.55	0.82	1.42
F	950	25.2	55.5	Hyper.	0.56	0.80	1.40

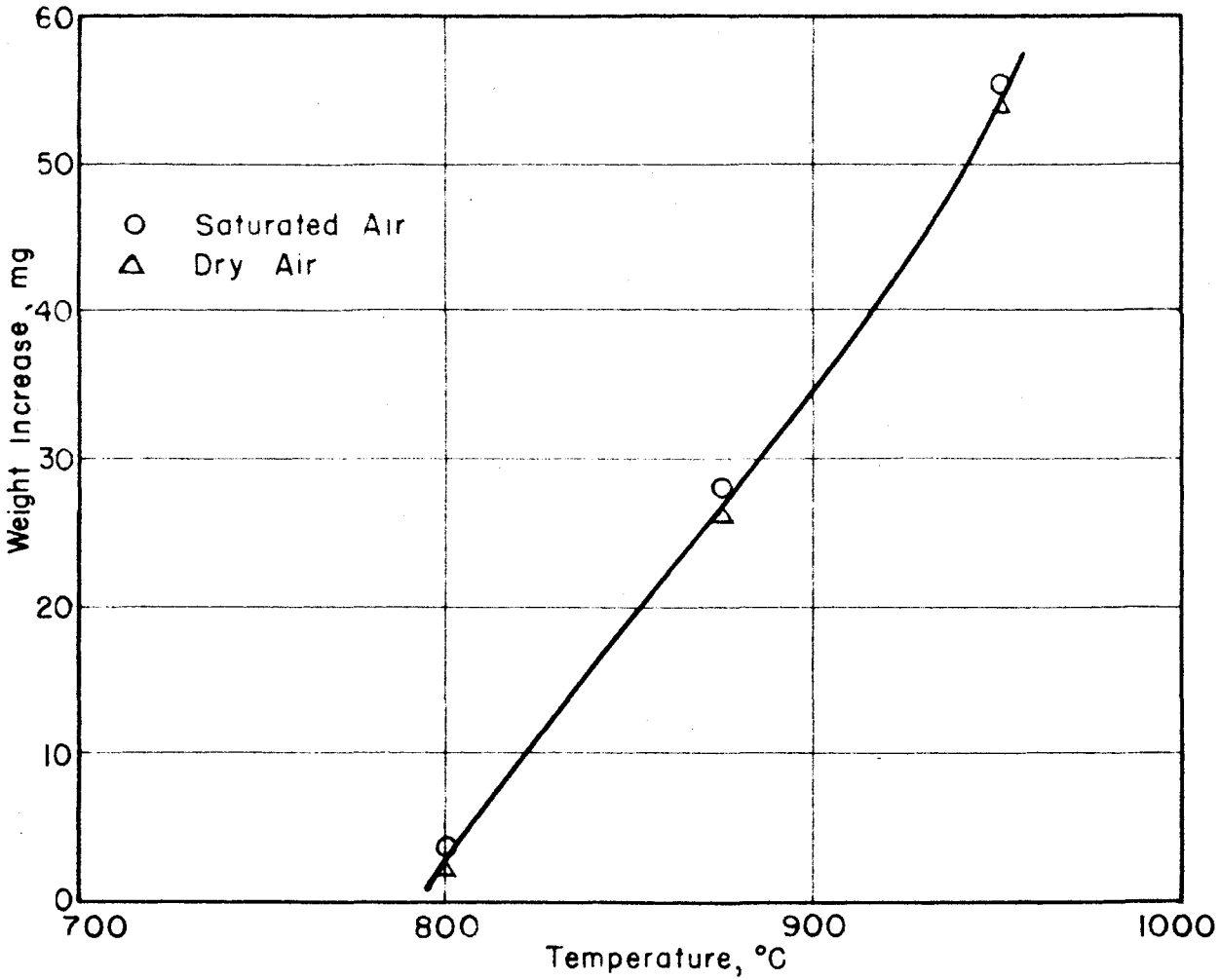


Figure XVIII. Curve Showing the Effect of Moisture on Carburization at various Temperatures. 4 Hours at Temp. 15 o/o $BaCO_3$ Pack.

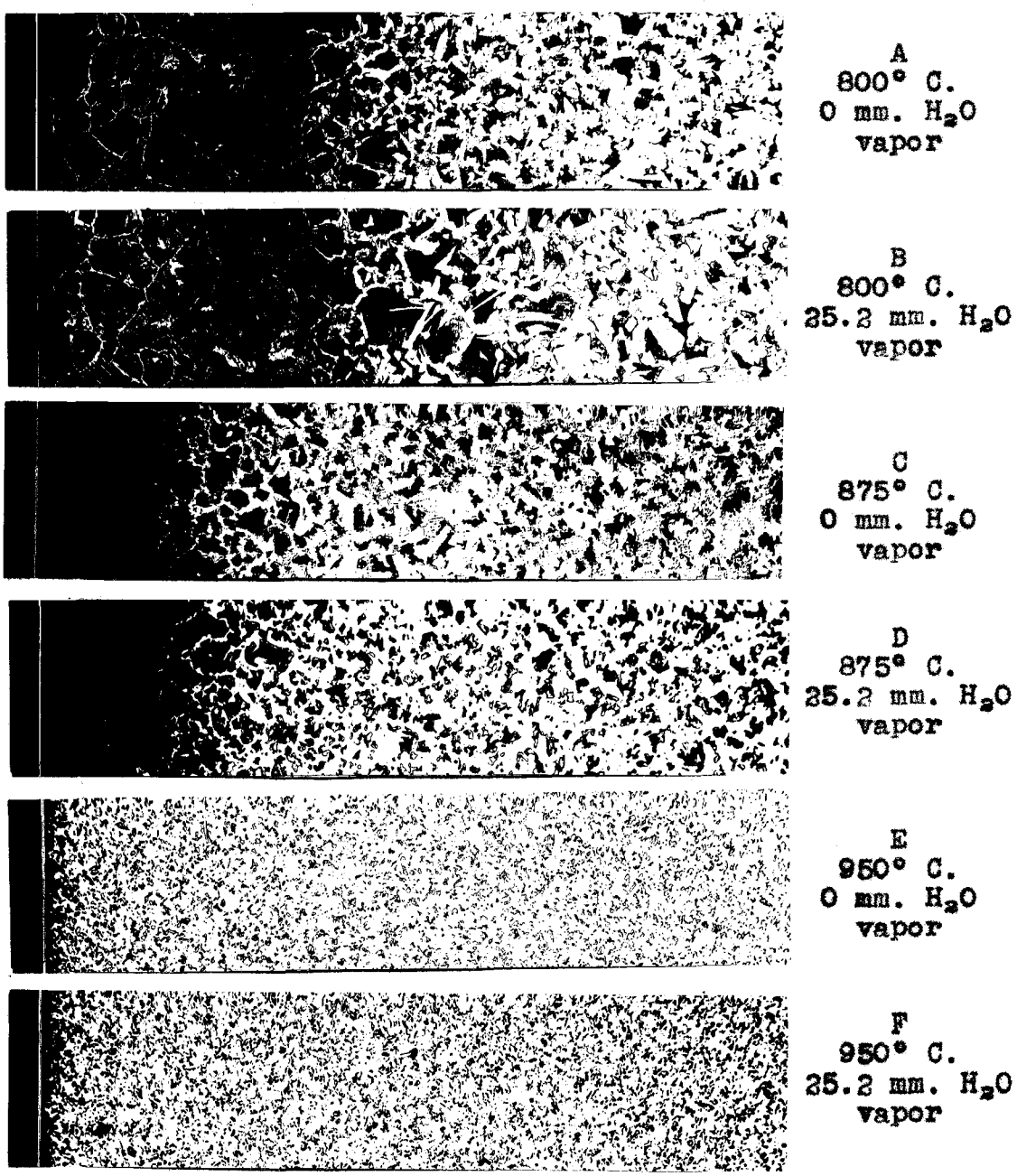


Figure XIX. Effect of 25.2 mm. H_2O Vapor on Carburization 4 Hours at Temp. Pack, 15 o/o $BaCO_3$. Surface of Sample Indicated by White Line at Left. X 50

The weight increase data, as well as the case depths, for the samples run at 950° C. were of the same order of magnitude as those obtained with the "vacuum" or low pressure carburization. This is also found by a comparison of the 800° C. samples. No decarburization was obtained at 800° C. when low pressures were used. This indicates that the carbon dioxide, which decarburized at this temperature with the sugar charcoal alone, was not present during the low pressure or "vacuum" runs. Also decarburization was not obtained at 800° C. using the energized pack. According to the theory of Ragatz and Kowalke (2), the function of the barium carbonate in preventing this decarburization would be to shift the reaction $2CO = CO_2 + C$ to the left and thus reduce the carbon dioxide concentration at equilibrium.

During the discussion of the variable pressure data, it was pointed out that the total depth of carbon penetration at atmospheric and down to 13 mm. pressure was nearly the same as it was at the lower pressures, even though the amount of carbon entering was much less. This same phenomenon is again evident when samples (G) and (H) (Table IV) are compared with samples (E) and (F) of Table V. The amount of carbon entering the samples during the carburization with the unenergized pack was much less than during the runs using the energized pack, yet the depth of carbon penetration was about the same. It was suggested in the previous discussion that perhaps this

phenomenon was due to some gas. The fact that the cases obtained at 950° C. with the energized pack are comparable to those obtained at the same temperature with low pressures seems to substantiate this hypothesis. If the carbon dioxide evolution theory of energizer action is used, the decomposition of the barium carbonate would replace this gas with carbon dioxide and carbon monoxide and thus it would not be available to aid in the carbon penetration. If either the theory of Ragatz and Kowalke (2) or that of Takashahi (33) is followed, the net result is still an increase in volume which would cause a displacement of the postulated gas. After this displacement of the gas has taken place, the carbon penetration would, as did at the low pressures, depend upon diffusion under increased carbon gradient. This explanation of the phenomenon under discussion is again only in the form of a hypothesis and suggests the need of considerable experimental verification. The comparable depths of case obtained for practically the same weight increase with the low pressure samples and the samples run in an energized pack indicates that perhaps the mechanism of carbon penetration is due to molecular migration and not to the carbon monoxide dissolving in the iron or steel.

V. SUMMARY AND CONCLUSIONS

A. Low Pressure or "Vacuum" Carburization

The results of carburization with sugar charcoal at reduced pressures may be summarized by the following facts and conclusions:

1. At 950° C. carburization was increased by reducing the pressure in the system, the largest rate of increase with change of pressure occurring at a pressure of about 12 mm. The amount of carburization was a maximum and almost constant for pressures between 5 mm. and the "vacuum" pressure. The cases obtained were normal.

2. With the conditions used, carburization took place with sugar charcoal at pressure below 20 microns. The carburization at low pressures was not inherent with the experimental conditions such as charcoal, steel, or containers. The carbon penetration was very sensitive with respect to the condition of the surface of the steel, the proper conditions being a fresh clean surface.

3. The "vacuum" or low pressure carburization increased in a logical manner with an increase in time or temperature.

4. The depth of penetration at pressures between atmospheric and 12 mm. was approximately the same as for the lower pressures, even though the amount of carbon in the case

was considerably less. An hypothesis has been suggested that the penetration at the higher pressures may be due to the action of a gas which aids in the penetration, even though the carbon gradient is low. The verification of such an explanation, however, would require considerable experimental investigation.

5. The "vacuum" or low pressure carburization was obtained at pressures considerably lower than those used by previous investigators, who reported either very slight or negative results. The explanation for their results could lie in the condition of the surface of the steel used.

6. Since good carburization took place at pressures below 20 microns, it is hard to conceive that the small amount of gas left could account for the process. It is concluded that the direct action of carbon with iron takes place under the conditions of the investigation. The carbon may dissolve directly in the austenite or Fe_3C may be formed and this dissolves and diffuses inward. The poor carburization obtained at the higher pressures could be due to the fact that the gases present prevent the direct interaction of the carbon with the iron.

7. Since this high carbon absorption took place at low pressures, and then only through fresh clean surfaces, the method is of limited importance in the practice of carburization.

B. Moisture Studies

The investigations on the effect of moisture (up to 25.2 mm. H_2O vapor) on carburization with sugar charcoal alone and with a 15 o/o barium carbonate energized pack may be summarized as follows:

1. In sugar charcoal alone, the samples run at 950° C. and 875°C. using air saturated at 25° C. showed, on the average, about 1 mg. greater gain in weight than samples run at the corresponding temperatures using dry air. The cases obtained using saturated air showed slightly less ferrite extending to the edge of the samples than did the cases obtained using dry air.

2. Samples run in sugar charcoal alone were decarburized at 800° C., the amount of decarburization not being affected by the moisture content of the air used.

3. With a 15 o/o barium carbonate energized pack the samples run at 950°, 875°, and 800° C. using saturated air showed about 1 mg. greater gain in weight than the corresponding samples obtained when using dry air. No difference in case characteristics was noticeable.

4. The case obtained at 950° C. with the energized pack was about the same as that obtained at the same temperature with the "vacuum" carburization.

5. The depth of carbon penetration in the unenergized charcoal was approximately the same as that in the energized

pack, even though the amount of carbon in the case was much less. This phenomenon was brought out in the study of variable pressures. Since the cases obtained at 950° C. in an energized pack and those obtained at the same temperature with the "vacuum" carburization were comparable, it was suggested that this substantiates the hypothesis that some gas aids in the carbon penetration when air is present.

6. The presence of the energizer prevented decarburization at 800° C. It is concluded that the CO_2/CO ratio is decreased by the energizer. No decarburization occurred at this temperature during the "vacuum" carburization because of the absence of carbon dioxide.

VI. LITERATURE CITED

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